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RADIOLOGICAL DECONTAMINATION
OF DRINKING WATER
BY ION EXCHANGE

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(C) RADIOLOGICAL DECONTAMINATION OF DRINKING WATER BY ION EXCHANGE

A Literature Survey and Report on an Investigation of
The Behavior of Yttrium-91 and Barium-Lanthanum-140,

Prepared for

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PREFACE

The appearance of commercial water-decontamination kits attests to the important position water contamination occupies in the thoughts of the general public. While many authorities in the field of civil defense believe that radiological decontamination of drinking water should be given a low priority among radiological civil defense measures, none deny that contingencies may arise in which the availability of sufficiently decontaminated drinking water would tend to increase significantly the life-span of its users and, in many cases, prevent the occurrence of acute symptoms caused by the ingestion of radioactive materials. The greater the proportion of the population protected by fallout shelters becomes, the greater the relative value of decontaminated air and water.

Conventional water treatment processes generally may not be relied upon to remove radioactive contaminants from water to an extent sufficient to render it safe for drinking purposes. While modification of existing, or installation of auxiliary, treatment facilities and processes on a large scale may be too costly to be practical, the special treatment of only the relatively small portion of water destined for drinking and culinary purposes would appear feasible. Such treatment could be performed near the point of consumption, either at community distribution stations or in the individual household. Besides providing adequate decontamination, the procedure should require only readily available equipment, and utilize inexpensive consumable materials.

Among the various methods suggested for small-scale decontamination, those using the principle of ion-exchange best satisfy these requirements. It is the objective of the present report to study the feasibility and effectiveness of ion-exchange processes for the radiological decontamination of water.

This task has been attacked by reviewing the pertinent theory and the results of specific studies concerning the removal of the radioisotopes considered most important as internal contaminants. Experiments were then designed to throw light on the difficulties that arise in decontamination by ion exchange as a result of the tendency of certain radioactive ions to undergo complex formation with hydroxide ion. The isotopes studies in this connection were Y^{91} and $Ba^{140}-La^{140}$.

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I. INTRODUCTION

Numerous studies [1-7] have indicated that in the period following a nuclear attack, conventional water treatment processes can not be relied upon to remove radioactive contamination from water sufficiently to render it generally safe for drinking purposes. Modification of the existing, or installation of auxiliary treatment facilities and processes on a large scale, would appear too costly to be practical. The possibility has therefore been suggested [8] of specially treating only the relatively small portion of water destined for drinking and culinary purposes. Such treatment would be performed near the point of consumption, either at community distribution stations or in the individual household, and should satisfy the following specifications:

1. Decontamination should be adequate.

2. It should be simple to improvise the required equipment from readily available stock items.

3. Any consumable materials needed should be readily available or inexpensive and easily stored.

4. The system should not depend on electrical power for its operation.

5. A minimum of skill should be required of the operators.

Some of the methods suggested for small-scale decontamination of water include precipitation or coagulation, sedimentation, filtration, and ion exchange; and special methods, such as distillation and electrodialysis.

As will be seen from the discussion in Chapter II, ion exchange meets the criteria listed more completely than any of the other methods. Its potential application ranges from the large-scale ion-exchange water treatment plant to the slurrying of water with clay or soil shaken in a jar. The principle is the same; ions originally present in the water replace ions attached to the solid. For the greatest decontamination efficiency the exchanger is packed into a column through which the contaminated water passes. Ion-exchange resins are not inexpensive, but small quantities may suffice to purify the most urgently needed water. Furthermore, studies of household water softeners have given indication that they may afford a significant measure of decontamination [5], and such ubiquitous substances as soils and clays may provide ion-exchange materials at low cost [9]. The equipment is equally simple. Any nearly cylindrical container with openings at either end may be suitable--a household water softener being an example of such a container available in many cases. However, smaller containers would be adequate under most circumstances. Modern ion-exchange resins may be stored without deterioration for prolonged periods of time, and the chemical engineering technology of the process is available in an advanced state of development [10-12].

OBJECTIVES AND SCOPE OF INVESTIGATION

The general objective of the research reported herein was to provide a basis for the design of ion-exchange systems for small-scale decontamination of drinking waters following a nuclear attack. This was done by collating existing data on the ion exchange of radionuclides of disaster health significance and supplementing these data with appropriate laboratory studies.

The uptake of radioactive substances present in ionic form and in trace concentrations is governed by a well-developed theory on the performance of ion-exchange columns as outlined in Chapter III. On this basis the principles underlying the numerous data on the decontamination of various radioactive solutions can be discerned and applied to the present problem when the respective articles contain sufficient information to define the variables involved. The problem is somewhat simplified by the fact that the presence of one trace component has no effect on the others, and that in small-scale decontamination the admissible flow rates may be so low that they lead to simulation of the ideal case, i.e., when equilibrium exists at any time of the operation and at any point in the column.

Comparison of the degree of decontamination actually achieved with that to be expected theoretically, especially in columns filled with equivalent mixtures of strongly acidic and strongly basic ion-exchange resins (mixed-bed columns), reveals that the actual degree of decontamination falls far short of expectations in many cases. Such cases generally involve the presence of radionuclides existing partially, or entirely, in anionic or non-ionic forms, the latter materials being capable of penetrating through deep mixed beds.

Inasmuch as the most critical radionuclides from the standpoints of health and ease of removal, determine the design of a decontamination column, the experimental studies performed under the present contract have centered on isotopes, or genetically related isotope pairs, that exhibit such anomalous breakthrough behavior, while also being hazardous fission products. The nuclides selected were Y^{91} and $Ba^{140}-La^{140}$. Both yttrium and lanthanum are known to exist in anionic forms--a tendency that increases with the pH level. At some intermediate pH values, the existence of non-ionic forms is also probable.

The ion-exchange materials used in these studies were: a greensand; a typical, strongly acidic modern cation-exchange resin; a strongly basic anion-exchange resin; and a number of California soils. The water composition characteristics examined included hardness, and sodium and hydrogen-ion concentrations. The work included equilibrium studies, performed with batches of the ion-exchange material in contact with various solutions, and studies of column performance. In the latter, contact time was the principal operational variable investigated.

NEED FOR RADIOLOGICAL DECONTAMINATION

Assessment of the desirability of radiological decontamination depends on the reduction of hazard achieved and on the cost, or human effort, involved in the decontamination measures. Also of importance may be the possible detraction of attention from more vital pursuits at a time of extreme emergency.

The question whether supplies of drinking water are likely to become "excessively" contaminated in the event of a nuclear attack has been discussed by Kaufman and Dennin [8], Woodward and Robeck [13], Clarke, et al. [14], and Hawkins [15, 16]. The problem is linked with so many unknowns that a definitive solution does not seem possible. Not all sources of drinking water are likely to become unacceptably contaminated, and those that do may be expected to contain mixtures of radionuclides of highly variable composition, due to selective removal of certain fractions by the environment. Even if the composition of the radionuclide mixture were known, the effect of the presence of each nuclide in the body, especially the long-term effect, would not be certain, due to the unpredictable influence of the many factors involved. Another area of uncertainty is the level of biological damage that can be considered acceptable under the conditions of a nuclear war.

Inasmuch as an early resolution of these problems is not likely, the maximum permissible emergency levels proposed by the then Federal Civil Defense Administration [17] may be used as a guide. These levels are shown in Table I.

TABLE I

EMERGENCY LEVELS OF RADIOACTIVITY IN WATER [17]

Consumption Period		Type of Activity	Emergency Level $\mu c/ml$
Time After Attack	Duration days		
First month	10	Beta-gamma	0.09
	30	Beta-gamma	0.03
Any time	10	Alpha	0.005
	30	Alpha	0.0017

In spite of the difficulties mentioned, it is useful to search for those isotopes which will probably constitute the most significant health hazards as radioactive water contaminants. When a number of such nuclides have been selected, the effectiveness of a decontamination procedure can be measured, relative to their removal, with far more significance than merely on the basis of reduction in total or gross radioactivity concentration. A method of estimating the relative importance of the major isotopes occurring in radioactive fallout is presented in the following section.

RELATIVE HAZARD OF FISSION-PRODUCT RADIOISOTOPES

While total activity may serve as a rough index of the hazard of ingested radionuclides contained in water (based on the dose absorbed by the lining of the gastrointestinal tract), the concentration of individual isotopes must be used as the criterion of radiotoxicity relative to other organs. Kaufman and Dennin [8] have presented a table of the most

hazardous radioisotopes likely to occur in fallout, based on peacetime maximum permissible concentrations and the relative prevalence of the isotopes in a fission-products mixture. These data, which were intended only as a preliminary estimate, can be refined by taking the radioactive decay of the individual fission products into account, as Teresi and Newcombe [18, 19] have done. These authors have computed 90-day and shorter-term doses for 14 isotopes selected as the most hazardous of a fission-products mixture corresponding to the data of Hunter and Ballou [20], but including an amount of Np^{239} such that its activity corresponds to sixty per cent of the total activity four days after burst.

The calculated 90-day doses imparted to the kidneys by Ru^{103}, Ru^{106}-Rh^{106}, Te^{127}, and Te^{129}, and to muscle tissue by Cs^{137}-Ba^{137}, due to intake of the Teresi-Newcombe fallout mixture at various times up to one year after blast, are relatively insignificant. Much larger are the doses, as shown in Table II, to the bone by Sr^{89}, Sr^{90}-Y^{90}, Zr^{95}-Nb^{95}, and Ba^{140}-La^{140}; and to the thyroid by I^{131}.

TABLE II

90-DAY RADIATION DOSE TO BONE AND THYROID

Beginning of Intake, days after burst	Radiation Dose in Rem[a]									
	Bone									Thyroid
	Sr^{89}	Sr^{90}-Y^{90}	Y^{91}	Zr^{95}-Nb^{95}	Ba^{140}-La^{140}	Ce^{144}-Pr^{144}	Pm^{147}	Np^{239}	Total	I^{131}
0.5	15.8	0.5	0.0	4.8	7.9	0.0	0.0	0.0	29.0	100
1	30.0	0.9	0.0	9.4	15.0	0.0	0.0	0.0	55.3	183
2	56	1.8	0.1	18.1	26.8	0.0	0.0	0.0	103	341
4	107	3.5	0.1	35.7	45.4	0.1	0.0	0.0	192	600
7	218	6.8	0.3	68	83	0.2	0.0	0.0	376	938
14	682	24.6	0.9	218	192	0.6	0.0	0.0	1118	1810
28	1364	60	1.8	468	214	1.3	0.0	0.0	2109	1362
105	2308	268	3.3	881	15.2	5.0	0.0	0.0	3480	7.5
210	1500	750	2.5	833	0.1	10.0	0.1	0.0	3096	0.0
365	556	1900	1.0	417	0.0	18.5	0.2	0.0	2893	0.0

[a] Based on ingestion of Teresi-Newcombe mixture of 1 μc/ml at indicated time after burst.

Perhaps a lifetime dose and corresponding intake period would be more realistic than the 90-day dose and intake period. Using 50 years as the average remaining life-span of the population, such doses were computed for the same bone and thyroid seekers as were listed in Table II. The assumed composition of the fallout mixture was identical to that used by Teresi and Newcombe, except that the more recent Löw and Björnerstedt computation [21] for the composition of a fission-products mixture, and health physics constants summarized by the International Commission on Radiological Protection were used. The fallout mixture was assumed to be two days old at the beginning of intake.

The results of these dose computations show Sr^{90} plus Y^{90} to be by far the most important contributors for the life-time bone dose, with Sr^{89} and Ba^{140}-La^{140}, respectively, contributing doses two and three orders of magnitude smaller. The dose to the thyroid is relatively large, approximately forty times that to the bone. Comparison of Tables II and III shows that injudicious use of relatively short-term doses can lead to considerable variation in estimating the doses likely to be received.

TABLE III

50-YEAR RADIATION DOSE TO BONE AND THYROID

Isotope	Dose, Rem[a]	Percentage of Total
BONE		
Sr^{89}	131	1.5
Sr^{90}-Y^{90}	8800	98.4
Y^{91}	0.063	0.0
Zr^{95}-Nb^{95}	0.014	0.0
Ba^{140}-La^{140}	8.8	0.1
Ce^{144}-Pr^{144}	0.24	0.0
Pm^{147}	0.015	0.0
Np^{239}	0.005	0.0
Total	8940	100.0
THYROID		
I^{131}	3.2×10^5	---

[a]Based on ingestion of Teresi-Newcombe mixture containing 1 μc/ml 48 hours after burst.

II. THE FEASIBILITY AND BENEFITS OF DECONTAMINATION

The principal methods entering into consideration for the radiological decontamination of drinking water are precipitation, filtration, distillation, electrodialysis, and ion exchange. In addition, water relatively free of radioactive contamination may be attained through the development of ground water sources where natural filtration and ion exchange combine to provide highly effective decontamination. Even storage, either in lakes or artificial impoundments, may serve to bring about a significant decontamination through sedimentation and decay.

A majority of the conventional municipal water treatment facilities are designed to remove only particulate matter, such as bacteria and suspended clay and silt particles, and have very limited decontamination capabilities for the mono- and divalent cations. As early fallout is associated with relatively large particulates, the majority of municipal treatment systems should provide some removal of radioactivity. However, certain of the physiologically important isotopes, such as those of strontium and cesium, may arrive in water as small soluble oxide particles and may thus appear at the treatment facility in an ionic form. Hawkins [16] has reviewed the efficiencies of municipal processes for fallout removal and his findings have been summarized in Table IV. In the case of water softening involving the precipitation of calcium carbonate, generally increased calcium removals are accompanied by improved strontium decontamination, but removals above 90 per cent are unlikely except with waters having an initial hardness in excess of 300 mg/l. It is conceivable that a municipal plant could employ phosphate softening as an emergency measure and perhaps increase strontium removals to 95 per cent, but this approaches the maximum capability of the conventional plant unless additional and costly facilities are installed.

Distillation plants may be relied upon to provide a high degree of radiological decontamination as well as to render innocuous biological, and possibly certain chemical, warfare agents. Lacy and Lundsten [22], using a 1,200 gpd thermocompression distillation unit, obtained decontamination factors ranging from 350 to 5,000 for waters containing I^{131} or various fission-product mixtures. With a de-entrainment device, these factors were generally improved by an order of magnitude. Unfortunately, distillation plants in existence are all too few to provide a significant portion of municipal water needs, even under an emergency situation where requirements are minimal. Furthermore, it is doubtful if such plants would continue to function in the immediate post-attack period when the greatest degree of decontamination might be needed. Distillation on any significant scale by the individual householder would appear to be highly impractical considering the many constrictions of the post-attack period.

Joint studies by the Oak Ridge National Laboratory and the Robert A. Taft Sanitary Engineering Center, U. S. Public Health Service [23] have shown that electrodialysis with perm-selective membranes is not effective in removing the colloidal fraction of radio-contaminants from water. Even preliminary filtration through a millipore filter failed to provide full

removal of Ru^{103} and Ce^{144}-Pr^{144}. In addition to its limited effectiveness for radiocolloids, it is doubtful if electrodialysis represents a practical solution to emergency water decontamination, especially for small-scale home operations. A limited number of industrial plants are operating on this principle to deionize brackish water, but since they require a sizable initial investment and need electrical power for operation, they cannot be seriously considered for nuclear disaster situations.

TABLE IV

ANTICIPATED EFFECTIVENESS OF CONVENTIONAL WATER TREATMENT
PROCESSES FOR THE REMOVAL OF FALLOUT
Hawkins [16]

Type of Water Source	Treatment Process	Approx. Quantity of Chemicals[a] grains/gal	Percentage of Activity Removed	
			Dissolved Activity	Activity on Suspended Matter[b]
RESERVOIR: Low turbidity and intermediate hardness	Alum coagulation and sand filtration	2	25-50	50-75
	Iron coagulation and sand filtration	2	25-75	50-75
	Lime-soda softening and sand filtration		50-75	50-90
RIVER: Intermediate turbidity and hardness, such as Ohio or Tennessee Rivers	Alum coagulation and sand filtration	3	30-80	50-90
	Iron coagulation and sand filtration	3	30-80	50-90
	Lime-soda softening and sand filtration		50-80	60-95
RIVER: High turbidity and intermediate hardness, such as Potomac River	Alum coagulation and sand filtration	5	35-85	50-90
	Iron coagulation and sand filtration	5	35-85	50-90
	Lime-soda softening and sand filtration		50-90	75-98

[a]Excess chemicals will somewhat increase removal of both suspended and dissolved material, while 200 ppm excess soda-lime will increase strontium removal to 75-90 per cent.

[b]Considered to be mostly 5 μ material with a maximum size of 20 μ.

CHARACTERISTICS OF SMALL-SCALE ION
EXCHANGE SYSTEMS

Ion exchange systems have a number of advantages over the decontamination processes previously discussed, especially for small-scale or individual applications. With the exception of distillation, ion exchange provides the highest degree of decontamination. Furthermore, the process can be developed on a small scale with practically no investment in equipment and can be operated with reasonable effectiveness by individuals with no knowledge of water treatment. Since in emergency situations regeneration would be undesirable, and probably unnecessary, the operation of an ion exchange system could be reduced to the act of pouring water through a column. In an emergency any garden soil could serve as the exchange medium. However, to insure water of better physical quality and to improve the hydraulic properties of the exchanger column, granular natural or synthetic exchange materials would be more suitable.

The compact nature of a single service (non-regenerative) ion-exchange unit can be illustrated by a simple calculation. A column 6 inches in diameter and 24 inches in length would contain approximately 0.4 cu ft of exchanger. If a typical strongly acidic nuclear sulfonic acid resin was employed the exchange capacity would amount to about 16,000 grains of $CaCO_3$. Assuming the unit were to operate on a sodium cycle and that softening to remove calcium would effectively remove the strontium isotopes, it would then be possible to decontaminate approximately 1,000 gal of water having a hardness of 250 mg/l. The cost of the resin for such a unit would be about ten dollars and the container, if constructed of waxed cardboard, should cost no more than a few cents. The cost of storing a thousand gallons of water would be far greater than this. Mixed resin beds providing full deionization would be more effective, as will be discussed in a subsequent chapter, and would be two or three times more costly, yet would remain within the range of feasibility. Less costly exchangers--certain of the mineral exchangers, for example--are available, but as these have a lesser exchange capacity per unit volume some of the advantages of compactness would be lost in using them in preference to the high capacity resins.

The theory of ion exchange and its practical limitations for water decontamination will be discussed in the next chapter. However, it may be observed here that the ion exchange process is reasonably effective in comparison to other methods. Moreover, ion exchange is obviously more suitable for home application than any of the other methods considered herein or known to the authors. We may thus conclude that such systems are indeed feasible.

RADIOLOGICAL PROTECTION AND SHORT-TERM
WATER DECONTAMINATION

The desirability of a particular radiological countermeasure depends not only on its technical feasibility or capability of performing some specified task at acceptable cost, but also on the contribution of that task to radiation protection when compared with other countermeasures and their contributions. Thus, a judgement on the desirability of a countermeasure should be based on its relative feasibility-effectiveness.

The question "What does water decontamination really accomplish?" will be examined briefly, although the full exposition of this matter is considered to be beyond the scope of this report.

The benefits derived from reducing the intake of various radioisotopes by either lowering their concentration in water or shortening the period of exposure can be appreciated by an examination of Tables II and III. Decontaminating water for a certain period after a nuclear attack is equivalent to delaying the beginning of the intake period. Inasmuch as Sr^{90}-Y^{90} are the major contributors to the lifetime bone dose, and noting that their decay is nearly negligible in comparison with the other nuclides, an initial period of decontamination will reduce the long-term dose in proportion to the reduction of strontium intake. Thus, short-term decontamination for the removal of Sr^{90} does not make a significant contribution to the reduction of the lifetime dose. In this case permanent, rather than emergency measures, are indicated. However, Sr^{89}, Zr^{95}-Nb^{95}, and Ba^{140}-La^{140}, having half-lives of 54 days, 63 days, and 12.8 days, respectively, make a relatively significant early contribution to bone dose that may be eliminated by short-term water decontamination as an emergency measure.

In comparison with the bone-seeking radioisotopes, the thyroid dose from I^{131} is relatively large, suggesting that the removal of this isotope on a short-term basis would also be beneficial. This is especially true due to the short half-life (8.3 days) of I^{131}. For example, a two-month iodine decontamination period would achieve better than a one-hundred-fold reduction in life-time thyroid dose.

Another question that should be examined is the total reduction in lifetime dose to the gastrointestinal tract as a function of short-term emergency decontamination. This relationship may be estimated by assuming the applicability of the Teresi-Newcombe mixture, that decay is in accordance with the "1.2-law," and that the weighted average effective energy of the mixture is constant. Under these circumstances, decontamination during the initial post-attack month would reduce the lifetime dose by about 50 per cent, whereas a six-year period of decontamination would be required to achieve a 90 per cent reduction. Because the cells lining the gastrointestinal canal are rapidly replaced, the dose-rate is probably a more valid criterion than the total integrated dose.

The effect of postponing the beginning of intake on the maximum dose rate is another means of judging the merit of early short-term decontamination of water. In the case of Sr^{90}-Y^{90}, the maximum dose rate occurs after 19 years of continuous intake. Short-term decontamination would have little influence on this rate. In contrast, the decay of I^{131} is sufficiently rapid that short-term decontamination would provide a significant reduction in the thyroid dose rate. With regard to the gastrointestinal canal, decontamination for 100 days, i.e., delaying initiation of intake for this period, would reduce the dose rate by a factor of approximately 100.

In summary, it may be stated that the effects of fallout nuclides in the body are likely to be manifested most strongly in the gastrointestinal canal, the thyroid, and the bone tissue. Other organs appear to

receive relatively low doses or dose rates. For short-term intake of relatively fresh fallout in water, Sr^{89}, Zr^{95}-Nb^{95}, and Ba^{140}-La^{140} contribute most significantly to the bone dose and are thus of interest with regard to short-term decontamination. I^{131} is also of greatest significance in terms of the short-term intake situation. In the gastrointestinal tract up to one month after burst, I^{131}, followed by Ce^{144}-Pr^{144}, Y^{91}, and Zr^{95}-Nb^{95} make the greatest contribution and are indicated as radionuclides that might be justifiably removed from water.

III. THEORY AND PRACTICE OF ION EXCHANGE

An ion-exchange reaction consists of the exchange of ions in a liquid phase for an equivalent number of ions carrying a charge of the same sign in a solid phase. The material in the solid phases capable of participating in such a reaction is called a cation or anion exchanger, depending on the sign of the charges of the ions involved. The maximum amount of ions that can be exchanged per unit quantity of the exchanger is a constant characteristic of the exchanger material and is called the ion-exchange capacity.

Owing partly to historical accident and partly to the ability of synthetic organic chemistry to prepare a great number of ion-exchange materials, the description of these materials and their properties has·become complex. The nomenclature is further complicated by a number of trade names whose connection with specific chemical structures is not always easy to establish. For the purpose of the present study, however, it will suffice to describe the few types of ion-exchange materials employed in the majority of modern installations, and those of their properties that have direct bearing on the problem of the removal of trace concentrations of certain ions.

Among the first types of cation exchangers used for water softening were the greensands or glauconites, which are still employed on a limited scale today. They are iron-aluminosilicates containing exchangeable potassium ions. The openings in the relatively rigid space-lattice are so small that ion exchange can take place only on the crystal surfaces, which accounts for the relatively low exchange capacity of approximately 0.15 me/g of sand. Greensands are chemically unstable at low pH and can not, therefore, be regenerated into the hydrogen form.

Most of the now far more widely used organic ion-exchange resins consist of an elastic matrix of crosslinked polymeric chains to which certain functional groups are attached. These groups may be strongly or weakly acidic as, for example, sulfonic or carboxylic acid groups. The former are most commonly attached to divinyl-benzene crosslinked polystyrene matrices, while the latter are carried by polyacrylic matrices. A high degree of crosslinking stabilizes the resin chemically and mechanically, but tends to decrease the rate of the exchange reaction or to completely deny entry to large ions.

The exchange capacity of the sulfonic acid resins ranges from 3 to 5 me/g of dry resin, while that of the acrylic acid resins has nearly twice these values.

Modern, strongly basic, anion exchangers are generally produced by attaching quaternary amine groups to polystyrene-divinylbenzene matrices. Resins having trimethylammonium groups are usually classed as Type I; the slightly less basic ones having dimethyl, ethanol, and ammonium groups, as Type II. The exchange capacity of such resins ranges from 3 to 4 me/g of dry resin.

Weakly basic anion exchangers usually contain a mixture of primary, secondary, and tertiary amino groups. The resins may be synthesized by condensation (e.g., phenol-formaldehyde-type) or polymerization (e.g., polystyrene-type) reactions.

ION EXCHANGE EQUILIBRIA

An ion-exchange reaction may be represented generally by the equation

$$bA^a + aBR_b = aB^b + bAR_a \ , \tag{1}$$
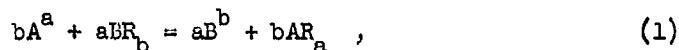
where A and B are ions of respective valences a and b of the same sign, and R is an exchanger suitable for the exchange of ions of this sign. The familiar softening reaction in which calcium is exchanged for sodium ion may serve as a specific example:

$$Ca^{++} + 2NaR = 2Na^+ + CaR_2 \ . \tag{2}$$
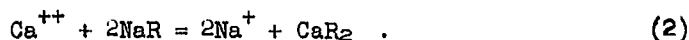
Such reactions are reversible. As an approximation, the mass-action law may be applied to them in the following form:

$$K_B^A = \left(\frac{q_A}{c_A}\right)^b \left(\frac{c_B}{q_B}\right)^a \ , \tag{3}$$

where c and q are the equivalent concentrations of the ions corresponding to the subscripts in the liquid and solid phases, in milliequivalents per milliliter or per gram of dry solid (in the hydrogen form for cation exchangers and the chloride form for anion exchangers), and K_B^A is the equilibrium coefficient for the reaction in the direction as written in Equation (1). The term "coefficient," rather than "constant," is used because its value varies with the ratio of c_A to c_B, or q_A to q_B, especially where the valences a and b are unequal.

Owing to the stoichiometric relationships in ion exchange, where only two species of ions are involved, the sum of the concentrations in the solid phase must equal the total exchange capacity Q, and the sum of the concentrations in the liquid phase equals the total concentration C. The relationships to be discussed below will be more easily handled if these conditions are used to eliminate c_B and q_B in Equation (3) to give

$$K_B^A = \left(\frac{q_A}{c_A}\right)^b \left(\frac{C - c_A}{Q - q_A}\right)^a \ . \tag{4}$$

Owing to the variability of K_B^A, the explicit definition of the equilibria between ions A and B and a particular exchanger requires a plot of K_B^A versus c_A/c_B or q_A/q_B. Since, as will be demonstrated below,

the value of K_B^A also depends strongly on the total solution normality when the valences of ions A and B are not equal, a number of such curves will exist for various values of C.

An alternative method of graphing is preferable in order to demonstrate the influence of C on the equilibrium based on the approximate validity of the mass-action law. For this purpose, one designates the fractional concentration c_A/C of A in the liquid phase by X and q_A/Q in the solid phase by Y. Equation (4) then becomes:

$$K_B^A \left(\frac{Q}{C}\right)^{a-b} = \left(\frac{Y}{X}\right)^b \left(\frac{1-X}{1-Y}\right)^q . \tag{5}$$

In the simple case of the softening reaction represented by Equation (2), this corresponds to

$$K_{Na}^{Ca} \left(\frac{Q}{C}\right) = \frac{Y_{Ca}}{X_{Ca}} \left(\frac{1-X_{Ca}}{1-Y_{Ca}}\right)^2 . \tag{6}$$

It is thus seen that, for any particular total solution concentration C, Y becomes a definite function of X. It can readily be observed that the uptake of the ion having the higher valency is favored at the lower total solution concentrations, for the lower the value of C becomes, the greater the value of $K_B^A (Q/C)^{a-b}$ becomes in Equation (5) (if a is greater than b). Since, for any value X_o of X, $Y^b/(1-Y)^a$ is equal to the constant

$$K_B^A \left(\frac{Q}{C}\right)^{a-b} \cdot \frac{X_o^b}{(1-X_o)^a} ,$$

it is clear that a decrease in C brings about an increase in Y. It is to this principle that water softening by ion exchange (at low concentrations) in conjunction with regeneration with sodium chloride (at high concentrations) owes its success.

Although regeneration is not considered practical in applications of ion exchange to civil defense decontamination problems, it is important to assess the effect of the total ionic concentration of the water to be treated on the tendency of multivalent ions to be removed.

Where more than two ionic species are present (multicomponent systems), Equation (5) still applies between each pair of species, but obviously the sum of the concentrations of all the species present, rather than of only two of them, is represented by C and Q.

The equilibria of ions present only in trace concentrations, such as the ions of radioactive contaminants, still conform to Equation (5), but may be used in a simplified form. If A is the trace ion, then X and Y become negligible compared to unity, and Equation (5) can be modified to obtain Equation (7);

$$K_B^A \left(\frac{Q}{C}\right)^{a-b} = \left(\frac{Y}{X}\right)^b \quad . \tag{7}$$

Plots of Y versus X are called exchange isotherms with the coordinates extending from zero to one. For values of $K_B^A (Q/C)^{a-b}$ equal to unity, the isotherm is the diagonal of the diagram and is also given by the equation Y = X. Isotherms lying above the diagonal are generally convex upward throughout and are said to correspond to "favorable" equilibria, while those below the diagonal are generally concave upward throughout and are associated with "unfavorable" equilibria.

EXCHANGER SELECTIVITY

The order of preference exhibited by an ion exchanger for various ions is called selectivity. The selectivity for ions of higher valence at low total solution concentrations has already been mentioned. It can be explained on the basis of the electric charge that the exchanger carries relative to the solution as a result of the Donnan potential. The greater the valence, the more strongly the charge attracts exchangeable ions, while the charge itself decreases with increasing solution concentration and decreasing exchange capacity.

Another important factor in determining selectivity is the radius of the hydrated ion. Ion-exchange resins are gels in which the tension on the not fully stretched carbon chains balances the swelling pressure. The greater the radius of the intruding hydrated ion, the greater the tendency to exclude it. This discrimination becomes more stringent as the degree of crosslinking increases, and consequently, the elasticity of the resin is reduced. Since for cations of elements in the same group of the periodic table, the hydrated ionic radius generally decreases with increasing atomic weight, the ions of the elements in such a group having the higher atomic weight are usually sorbed in preference to those of lower atomic weight. For the ions of the alkali metals, the selectivity of most cation-exchange resins thus increases in the following order: lithium, sodium, potassium, rubidium, cesium; and for the ions of the alkaline earth metals in the order: magnesium, calcium, strontium, barium. No such simple rule applies to anions.

The effect of hydrated ionic radius can sometimes be more than compensated for by the polarizability of certain ions in which the charge of the ion can be displaced towards its boundary to such an extent that the resulting electrostatic attraction towards the active fixed ionic groups of the exchanger becomes greater than that for ions of the same charge with a larger hydrated radius.

Owing to the sieve effect, ions exceeding a certain size may be completely excluded from the exchange sites in inorganic and highly crosslinked resinous exchangers. Although principally applicable to large organic ions, this effect may manifest itself with some of the larger anions of radioactive contaminants.

Specific interactions (between exchangeable ions and exchange sites) that can influence selectivity include association, such as

observed between hydroxide ions and weakly basic exchange groups, hydrogen ions and weakly acidic groups; chelation; and specific affinity of certain exchange groups for certain ions.

The sequence of affinities between a number of resinous ion exchangers and some of the more important cations is as follows: $Li^+ < H^+ < Na^+ < NH_4^+ < K^+ < Rb^+ < Cs^+ < Ag^+ < Tl^+ < UO_2^{++} < Mg^{++} < Zn^{++} < Co^{++} < Cu^{++} < Cd^{++} < Ni^{++} < Ca^{++} < Sr^{++} < Pb^{++} < Ba$ [24]. For anions, Kunin and McGarvy [25] have established the following approximate sequence: $F^- < OH^- < Cl^- < Br^- < NO_3^- < I^- < SO_4^{--}$. The position given for hydrogen and hydroxide ions in these series is that corresponding to strongly acidic or basic exchangers, respectively, For weakly acidic or basic resins, these ions are, of course, most strongly preferred by the resin over others.

COLUMN OPERATIONS

Ion exchange materials may be brought in contact with solutions in a number of ways, including batch-contact, fixed beds, and fluidized beds of various descriptions. Although numerous contacting schemes have been proposed in the literature, only the fixed beds or packed columns have found widespread practical application, especially in the field of water treatment. In such columns, the liquid passes up or down, usually the latter, through the packing. Flow rates in the order of 5 to 8 gpm/sq ft of column cross-section are common, but for decontamination on a small scale, much lower rates may be found practical and desirable. Bed-depths frequently range from 2 to 3 feet. As an approximation, the interparticle voids fraction may be taken as 0.4 for most types of column packing.

In order to visualize the progress of an ion-exchange operation carried out in a column, it is helpful to picture the concentration profiles of the various exchangeable ionic species in the column, as well as the histories of the concentrations of these species in the effluent. Very roughly, the concentration profile and concentration history for each ionic species will be mirror images of each other.

The time or effluent volume at which the concentration of an ion in the effluent rises beyond a specified fraction of the concentration of the same ion in the influent is called the breakthrough point. The part of the concentration-history curve covering the rise of the concentration of such an ion to its full influent concentration is referred to as the breakthrough curve.

The position of the breakthrough curve along the effluent-volume axis must be such that the area between it and the concentration axis equals the amount of the ion in question that has been accumulated in the column. This position is dictated by the composition of the influent water and the properties of the ion-exchange material, including its exchange capacity and, in multicomponent systems, selectivity. While the general position of the breakthrough curve is thus given under any set of conditions, its slope depends on a number of factors, some of which can be influenced by operating conditions such as flow rate.

Shapes of Breakthrough Curves

Extremely flat breakthrough curves are undesirable, not only because they reduce the effective or working capacity of a column, but also because they imply "leakage," i.e., the ion it is intended to remove appears in the effluent during operation of the column. The factors affecting the steepness of the breakthrough curve are associated with hydrodynamic phenomena attending the flow of the water through the column, diffusion, the equilibria involved, and the rate at which these equilibria tend to be established.

Dispersion of the zone between two ionic forms of the exchanger in the column, which finds its expression in an elongated breakthrough curve, can be the result of a spectrum of local flow velocities, crossing of flow lines, turbulence, channeling, and fingering. The last cause is associated with marked viscosity and specific gravity differences in the liquid phase and is thus not likely to play a role in the problem under study. Channeling may be the result of poor column packing or of contraction of the exchanger, which can become more serious in resins of low crosslinking. Dispersion in laminar and turbulent flow can be reduced by using lower flow rates, and these can be utilized in small-scale decontamination units in which the required rate of production is very low.

Less obvious than the causes named above is the effect of ion-exchange equilibria on the steepness of the breakthrough curve. It may be demonstrated by establishing a material balance between an infinitely thin lamina of the ion-exchange material and a small volume of solution passing through it that contains dN equivalents of ions of either charge. In the interest of simplicity, assume that the system is binary, and in order to exclude the complicating effect of kinetic considerations, that equilibrium is established instantly. Let A be the ionic species taken up, and X and Y the equivalent fractions of this species in the liquid and solid phases, respectively. Further, assume that the column cross-section is such that the lamina under consideration contains one equivalent of functional groups per unit length of packing.

Under these conditions, the solution will lose dXdN equivalents of ion A in its passage through the lamina, while the latter will gain dYdZ equivalents, where dX and dY are the differences between liquid and solid concentrations, respectively, at the end and beginning of the process, and Z the distance in the direction of the column axis. Since dXdN and dYdZ must be equal, it follows that

$$\frac{dN}{dZ} = \frac{dY}{dX} \quad , \tag{8}$$

or the content in ion A of one equivalent of resin was advanced from Y, in equilibrium with water of composition X, to Y + dY, in equilibrium with water of composition X + dX, during passage of solution containing dN equivalents of exchangeable ions through a distance dZ. If the flow rate in the column is held constant, then dN/dt, which is proportional to the flow rate, is constant. It follows that dZ/dt, or the rate of advance of the front of the saturated exchange material, must be inversely proportional to dY/dX, the slope of the exchange isotherm.

This observation leads to an important rule about the concentration patterns that establish themselves in ion-exchange columns in which the exchange of gross components takes place. If the exchange isotherm is convex upwards, then its slope is smaller at high than at low concentrations. A zone of low concentration will therefore tend to be retarded, while one of high concentration will move relatively faster, the result of these tendencies being a "self-sharpening" effect of the front.

The term "self-sharpening" does not imply that the concentration gradients in the zone in which exchange takes place becomes increasingly abrupt as this zone travels through the column, but merely that the disturbances already enumerated, and the diffuseness induced by equilibrium relationships at the beginning of the operation of the column, are counteracted by the "self-sharpening" effect, so that a constant concentration pattern develops in the column. The term "self-sharpening" owes its name to the increase in sharpness of the front relative to its distance of travel through the column.

The reverse argument explains why isotherms that are concave upward correspond to fronts that become increasingly diffuse--a pattern that has been termed "proportional" because the elongation of the corresponding breakthrough curves is approximately proportional to the column length.

The practical application of these rules is easy to see; in the case of self-sharpening fronts, the employment of longer columns leads to better utilization of the ion-exchange material, while in the proportional pattern case this advantage is not gained. The criterion determining which case applies for isotherms following Equation (5) is the value of $K_B^A (Q/C)^{a-b}$; if it is greater than unity, the isotherm is convex upward; if less, the isotherm is convex downward. The corresponding equilibria are said to be "favorable" and "unfavorable," respectively.

A rare intermediate case is characterized by the value of unity for $K_B^A (Q/C)^{a-b}$, but trace components, to which equations of the form of Equation (7) apply, also develop concentration patterns intermediate between the self-sharpening and the proportional.

The tardy establishment of equilibrium owing to diffusional resistances, either inside the exchanger particles or in the stationary liquid films surrounding them, tends to elongate the exchange zone. Theories taking into consideration kinetic effects, as well as the effect of equilibrium, have been presented by Thomas [26], Hiester and Vermeulen [27], and Glueckauf [28].

An important consideration in analyzing the probable development of concentration zones in columns is that near the top of a column the exchanger tends to establish equilibrium with the influent, while the effluent tends to be in equilibrium with the regenerated exchanger. Secondly, the general material balance equation;

$$\text{Equivalents entering column} = \text{equivalents leaving column} + \text{equivalents accumulated in solid phase and interstitial space} \quad , \qquad (9)$$

must be satisfied for all ionic species involved. In many cases, application of these principles based on a knowledge of the equilibrium coefficients involved permits an estimate to be made of the time of breakthrough of the various ions in the influent water.

INDUSTRIAL AND HOUSEHOLD ION-EXCHANGE ⸻
INSTALLATIONS

An examination of the principal types of water treatment installation employed by industry and in the household is of interest in connection with the possible employment of such units for decontamination purposes, and also because the principles illustrated can be applied to the design of units intended exclusively for decontamination.

In spite of growing industrial applications of ion exchange other than for water treatment, the latter still is the most important. The principal purposes of such treatment are softening, deionization, and the reduction of the scaling-potential of boiler feed waters. In large installations, softening by ion exchange frequently serves further to reduce the hardness of water that has already been treated by the lime-soda process.

According to their function, the most common types of ion-exchange water treatment installations can be classified into those that remove

1. calcium and magnesium ions,

2. calcium, magnesium, and bicarbonate ions,

3. all ions and carbon dioxide,

4. all ions, carbon dioxide, and other weak acids; and

5. all ions and weak acids and bases.

The divalent hardness cations are removed by an ion-exchange material in the sodium form. Although weakly acidic exchangers of the carboxylic acid or zeolitic type exhibit a higher selectivity for the hardness cations than do those of the sulfonic acid type, their regeneration requires such an excess of sodium chloride that generally the sulfonic acid resins are economically preferable. However, because of their low initial cost, greensands are still occasionally employed.

Calcium, magnesium, and bicarbonate ions can be removed by the so-called split-stream treatment, in which part of the water is passed through an exchanger in the sodium form, while the remainder passes through an exchanger in the hydrogen form, the relative amounts being so adjusted that the hydrogen ion liberated in the second column is sufficient to neutralize the bicarbonate ion contained in the effluent from the first.

For the removal of carbonic acid and all solutes present in ionic form, conventional de-ionization is used. In this process the water is first passed through a column containing a strongly acidic exchanger in the hydrogen form, then through a degasser, followed by a column containing a weakly basic exchanger in the hydroxide form. In the first column,

all cations are exchanged for hydrogen ion. Bicarbonate and carbonate appear in the effluent in the form of carbonic acid, which is removed by a degasser.

In the second column, the neutralization of the excess acid by hydroxide ions freed by the exchange of other anions greatly aids the equilibrium favoring that exchange, but undissociated weak acids pass through the column unchanged.

The exchanger in the first column must be strongly acidic to insure a sufficiently favorable equilibrium. A weakly acidic exchanger would hold the hydrogen ions too firmly to permit an effective exchange of other cations. In the following column, or columns, as much weakly basic anion exchanger as possible is used because of the greater efficiency with which it can be regenerated. As mentioned, the removal of hydroxide ion from the exchanger is aided by neutralization with the acidic effluent from the first column.

With complete regeneration of the exchangers, which is generally not economical, water having a conductivity of less than 10^{-6} mho/cm can be produced using conventional de-ionization procedures. Mixed-bed de-ionization is capable of further reducing this value by a factor of ten and thus is of special interest in decontamination work.

Mixed-Bed Systems

In this process, in which a mixture of equivalent amounts of a strongly acidic ion exchanger in the hydrogen form and a strongly basic ion exchanger in the hydroxide form are employed, all ions, including those of weak acids and bases, are removed. The main reasons why this type of installation has not found wider application are the technical difficulty created by the necessity of separating the resins before regeneration and the relatively low efficiency of regeneration; both considerations are of little importance in decontamination applications in which the resin is used only once.

The extraordinarily effective deionization achieved by mixed beds is due to the immediate mutual neutralization of the hydrogen and hydroxide ions replaced by the ions of the influent. The exchange equilibria are so favorably influenced that the level of regeneration has little effect on effluent quality, and breakthrough is very sharp.

IV. DECONTAMINATION BY ION EXCHANGE

Radiological decontamination of water by ion exchange has been the subject of recent papers published by various individuals and groups working at the Oak Ridge National Laboratory. These studies have generally involved artificially contaminated Oak Ridge tap water and the use of exchangers in either slurry or column systems. A brief review of this work will indicate the general potential of ion exchange as a decontamination process, and provide an introduction to the laboratory studies reported in Chapter V.

SLURRYING WITH NATURAL AND ARTIFICIAL EXCHANGERS

From consideration of material balances and equilibrium relationships, it can be shown that slurrying in either batch or continuous systems is far less effective than the application of the same exchangers in column systems. This limitation is especially evident for mono- and divalent radiocations in waters containing more than a few tenths of a milliequivalent of cations per liter. Thus Sr^{90} cannot be expected to be removed to any significant extent except with the application of enormous and impractical exchanger dosages. With the trivalent radiocations, and perhaps in certain instances with trace cesium concentrations, slurrying has some potential for decontamination, but only if the radiocolloidal problem does not arise. And even here, far better removals may be achieved by applying the exchangers in column systems.

The early work of Straub, et al. [2, 29], Brockett, et al. [30], Lacy [31], and that presented in the joint report of the Health Physics Division, O.R.N.L. and the Robert A. Taft Sanitary Engineering Center, U.S.P.H.S [23] lead to the conclusion that large volumes of clay must be employed and then subsequently handled as a semi-solid mass of contaminated sludge. The more significant results of the studies of Lacy and Lindsten [32] are summarized in Table V. The studies were conducted on Oak Ridge tap water with the analysis given in Table VI. The data given are based on a 15-minute contact period. However, extension to 90 minutes failed to materially improve decontamination. All samples were filtered prior to assaying.

DECONTAMINATION WITH ION EXCHANGE COLUMNS

In 1951, Ayres [33] reported on a study concerned with the application of ion-exchange resins to the treatment of radioactive wastes. He recognized the difficulty of sorbing such fission product isotopes as molybdenum, tellurium, and ruthenium on cation-exchange resins as due to their being present in largely the anionic form. He also observed that barium leakage through a column of strongly acidic cation resin decreased with the addition of only small amounts of carrier barium, a phenomenon that would appear to be contrary to the laws of mass action. A similar relationship was observed by Levin, et al. [34] for strontium and yttrium

TABLE V

DECONTAMINATION OF OAK RIDGE TAP WATER BY
SLURRYING WITH POWDERED EXCHANGERS
Lacy and Linsten [32]

Contaminant	Percentage Removed					
	Poly-styrene Divinyl Benzene (Permu-tit Q) Na-form[a]	Mixed Resin (Amber-lite MB-3)[a]	Green-sand[a]	Ben-tonite H-28[a]	Commercial Montmoril-lonite[a]	Oak Ridge Montmoril-lonite[b]
Ba^{140}-La^{140}		77-98				86-95
Ce^{141}, Ce^{144}-Pr^{144}	53-54					99-99
Cs^{137}-Ba^{137}		29-92				
Fission Products (40% Cs^{137})	61-76		46-63	75-81	60-68	59-63
Fission Products (48.5% rare earths; 20.4% Ce^{141})	51-84		52-66	57-76	50-70	
I^{131}		65-89				1-1
Pa^{233}	90-86	92-95	93-94	97-98	98-99	
P^{32}		17-89				
Ru^{106}-Rh^{106}						45-55[c]
Sr^{90}-Y^{90}	78-93		68-77	74-89	76-93	
Zr^{95}-Nb^{95}				98-99	99.3-99.9	94-99

[a]First figure of range given corresponds to 450, second to 2,700 ppm decontaminant.

[b]First figure corresponds to 1,000 ppm, second to 4,000 ppm decontaminant.

[c]3,000 ppm decontaminant.

TABLE VI

COMPOSITION OF OAK RIDGE TAP WATER

Ca^{++}	1.36 me/l	HCO_3^-	2.00 me/l
Mg^{++}	0.64 me/l	$SO_4^=$	0.18 me/l
Na^+	0.20 me/l	Cl^-	0.10 me/l

in exchanging with sodium resins. These authors observed removal to increase with ionic strength up to a value of approximately 0.1, and then to decrease, generally following the mass-action law.

Friend [35] studied the removal of Sr^{89} from Oak Ridge tap water by using one-foot beds of strongly acidic cation exchanger (Amberlite IR-120). A flow rate of 5 gpm/sq ft and 20-50 mesh resin particles were used. In the sodium form, the average decontamination factor (D_F) before breakthrough was 609, while in the hydrogen form an average D_F of 1,070 was observed. With mixed beds having lengths of 35 in. and operating on hydrogen-hydroxide and hydrogen-chloride cycles, decontamination factors of about 2,300 were observed. On a sodium-hydroxide cycle the D_F dropped to 944.

Lacy and Lindsten [32], also using Oak Ridge tap water and employing both single and mixed beds, studied the removal of Pa^{233}, Ta^{182}, Zr^{95}-Nb^{95}, and two fission product mixtures. The results of this work are summarized in Table VII. Leakage of the fission products and zirconium-niobium was considerable for the mono-cation bed operating on a sodium cycle, but somewhat less on a hydrogen cycle. The mixed beds were superior in every instance.

TABLE VII

DECONTAMINATION OF OAK RIDGE TAP WATER USING
MONO- AND MIXED-BED RESIN SYSTEMS[a]
Lacy and Lindsten [32]

Contaminant	Percentage Removal Before Breakthrough	
	Mono-Bed Strongly Acidic Cationic Resin Na-Form	Mixed Bed Strongly Acidic and Basic Resins H-OH Forms
Fission Products (40% Cs^{137})	70-86	92-99
Fission Products (48.5% rare earths; 20.4% Ce^{141})	70-89 (85-90 with H-cycle)	90-97
Zr^{95}-Nb^{95}	67-88	80-97
Ta^{182}	---	88-96
Pa^{233}	91-99	95-99.9

[a]Bed depth, 10 in.; flow rate, 6.5 gpm/sq ft.

Similar results were reported in the joint P.H.S.-O.R.N.L. study [23] and have been summarized in Table VIII. Although the operating conditions in this investigation differed somewhat from those of Lacy and Lindsten, the results are believed to be comparable, and in the case of $Zr^{95}-Nb^{95}$, removals are quite similar. As should be expected, monovalent Cs^{137} and divalent Sr^{89} are removed to the extent of 99 per cent or more by the cation exchanger, but to a negligible extent by the anion unit. However, Y^{91}, $Ba^{140}-La^{140}$, and $Zr^{95}-Nb^{95}$, although basically metals, are removed significantly on both types of resins suggesting both cationic and anionic properties. Of these isotopes, Y^{91}, La^{140}, and both Zr^{95} and Nb^{95} are known to form complexes or small radiocolloidal aggregates that may display negative charges. This is probably not the case with divalent Ba^{140}. Mixed resin beds are thus superior to either anion or cation beds operating singly or in series. Cation beds provided their greatest decontamination prior to calcium breakthrough, but continued to remove some Y^{91}, $Ba^{140}-La^{140}$, and $Zr^{95}-Nb^{95}$.

TABLE VIII

DECONTAMINATION OF OAK RIDGE TAP WATER USING
NATURAL AND ARTIFICIAL EXCHANGERS[a]
Joint O.R.N.L.-P.H.S. Study [23]

Contaminant	Percentage Removal Before Breakthrough			
	Strongly Acidic Cationic Resin Amb. IR-120 Na or H Form	Strongly Basic Anionic Resin Dowex 1 Cl or OH Form	Mixed Bed IR-120 and Dowex 50 H-OH Forms	Greensand Na-Form
Y^{91}	86-93	94-98	98-99	75
Sr^{89}	99.0-99.8	5-7	99.95-99.97	99.8
$Ba^{140}-La^{140}$	98-99	36-42	99.5-99.6	96
Cs^{137}	99.8	9	99.8	---
$Zr^{95}-Nb^{95}$	58-75	96.0-99.9	90.9-99.4	---

[a]Bed depth, 18 in.; flow rate, 2 gpm/sq ft.

Iodine Removal by Anion Exchange Systems

Friend's studies [35] also included an investigation of the removal of I^{131} from Oak Ridge tap water. The exchanger used in this work was Amberlite IRA-400, a strongly basic resin of the quaternary amine type with an exchange capacity of about one miliequivalent per milliliter of column packing. Bed depths were two feet and flow rates were generally about 5 gpm/sq ft. The results of these studies are shown in Table IX.

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TABLE IX

REMOVAL OF RADIOIODINE FROM OAK RIDGE TAP WATER
USING MONO- AND MIXED-BED SYSTEMS[a]
Friend [35]

Form of Exchanger	Bed Depth in.	Effluent pH	Percentage Removal
MONO-BED			
Cl	24	6.5-7.5	---[a]
OH	24	11.0	99.4
OH	24	11.3	98.9[b]
MIXED BED			
Cl-H	35	3.1	---[a]
Cl-Na	35	9.1	---[a]
OH-H	35	7.3	99.85
OH-Na	35	10.7	99.7

[a]Gradual breakthrough; removals not signifi-
cant.

[b]Flow rate, 7.5 gpm/sq ft; all others,
5.0 gpm/sq ft.

Under the neutral or acid conditions prevalent in the chloride
mono-bed and in the chloride-hydrogen and chloride-sodium mixed beds,
both iodide ion and molecular iodine are present, the latter being re-
sponsible for the gradual I^{131} breakthrough. However, under the alkaline
conditions created by resin in the hydroxyl form, the iodide ion predomi-
nates and I^{131} removals are high.

RADIOISOTOPE COMPLEXES

It is apparent from the experimental studies reviewed in this
chapter that at low concentrations many of the polyvalent cations form
complexes that behave as anionic or non-ionic aggregates. Only when
these cations are also radionuclides is it possible to observe these prop-
erties because at concentrations measurable by normal analytical chemical
methods the properties are not evident and the elements behave in a quite
different manner. It is quite possible that at low concentrations both
aluminum and yttrium have similar tendencies to form non-ionic aggregates,
but only in the case of the latter do we have an abundant supply of radio-
isotopes by which the aggregation property becomes observable.

Ray [36] has made a detailed review of the literature pertaining
to the behavior of the so-called "radiocolloids," a term applied to aggre-
gates causing anomalous characteristics of the polyvalent radionuclides.
Ray also studied the radiocolloidal properties of yttrium and indicated
that the complexes may have the form $[Y(OH)_i]^{n-i}$, when n is the valence
of the simple cation, i is the number of ligands of the complex, and n-i

is the valence of the complex. The ligands may range from zero to a number greater than n, the complex ion becoming anionic. In the case of yttrium the maximum number of ligands is estimated to be six. In the case of yttrium complex formation begins at a pH of about 4.5 and increases sharply above pH 6, the higher the pH the greater the number of ligands. Once formed, the yttrium complexes proved quite stable and were destroyed only slowly at pH 3 and below.

Helfferich [24] has presented an extensive review of ion exchange and sorption equilibria in the presence of complexing agents and has considered the general problem of ligand formation and sorption. He notes that potential ligands are ammonia, aliphatic amines, polyhydric alcohols, and anions of carboxylic and amino acids. Although the hydroxyl radical is not mentioned, it probably should be included. Anion exchangers have the greatest affinity for complexes of high ligand number, i.e., anions, whereas cation resins are more effective in sorbing complexes of low ligand number. Helfferich describes ligand exchangers as ion exchange resins containing complexing metal ions that have a strong affinity for the ligand. This suggests that cation exchange resins treated with aluminum ion might have a much greater capacity for the $[Y(OH)_i]^{n-i}$ complexes and thus lead to a reduction in yttrium leakage. In fact, aluminum conditioning of resins might enhance the removal of trace concentrations of all polyvalent cations that have a strong tendency to form hydrous oxides at low concentrations.

V. LABORATORY STUDIES

The general objective of the laboratory study was to ascertain the decontamination capabilities of several natural and artificial ion exchange media for the isotopes Y^{91} and $Ba^{140}-La^{140}$. The investigation employed both batch-type sorption equilibrium measurements and column systems that simulated the conditions that might be suitable for water decontamination in a post-nuclear attack situation. Batch systems have the advantage of simplicity and permit the screening of a variety of solute-exchanger combinations. However, such systems provide little indication of the leakage to be expected with columns or the extent to which trivalent radiocations and their associated radiocolloids may pass through exchanger columns.

MATERIALS STUDIED

The ion exchange media investigated included five representative California soils, a greensand, a strongly acidic cation exchange resin, and a strongly basic anion exchange resin. The soils were of the sandy-loam or sandy type, quite pervious, and widely distributed in California. Their characteristics are summarized in Table X. The greensand was a North American glauconite having an effective size of 0.38 mm and a uniformity coefficient of 1.95. The exchange capacity was 17.2 me/100 g as determined by using labeled calcium at room temperature. The greensand was used in its natural state with no pretreatment, except washing with distilled water to remove the finer material. When packed in a column this material had a void fraction of 0.41.

The ion exchange resins were obtained from the Chemical Process Co., Redwood City, California. The cation exchange resin (Duolite C-20) was an eight per cent cross-linked styrene divinylbenzene polymer with nuclear sulfonic acid functional groups and an exchange capacity of 4.9 me/g on a dryweight basis or about 1.8 me/ml of wet resin. The resin was supplied by the manufacturer in the sodium form and was used in this state except for those experiments with mixed beds in which it was converted to the hydrogen form. The anion exchange resin (Duolite A-101) was a highly porous, divinylbenzene cross-linked polystyrene with the trimethyl benzyl ammonium functional groups and an exchange capacity of 3.5 me/g on a dryweight basis or about 1.33 me/ml of wet resin. The anion resin was supplied in the chloride form, but was converted to the hydroxyl state before use. Both resins were spherical particles in the 16 to 20 U. S. Standard mesh range.

Four waters were studied: a relatively hard well water, a soft local tap water of surface origin, and two synthetic waters containing 5 me/l calcium and sodium chloride, respectively. The pH of these waters ranged from 6.1 to 8.4. Analyses of the two natural waters are given in Table XI.

TABLE X

CHARACTERISTICS OF CALIFORNIA SOILS

Soil Type	Yolo Sandy Loam	Hanford Fine Sandy Loam	Hesperia Sandy Loam	Columbia Sandy Loam	Oakley Sand
Parent Material	Sedimentary alluvium	Granitic alluvium	Granitic alluvium	Mixed alluvium	Wind-modified mixed alluvium
Soil Reaction	Neutral	Neutral	Neutral	Neutral	Slightly acidic
Effective Size,[a] mm	0.021	0.0074	0.0020	0.0033	0.020
Uniformity Coefficient[b]	8.1	24.9	67.3	47.3	11.2
Percentage Clay and Silt	22	27	38	34	14
Exchangeable Cations:					
Monovalent, me/100 g	0.43	0.72	0.89	0.51	0.24
Divalent, me/100 g	13.98	5.66	8.02	5.67	2.79
Total Exchange Capacity, me/100 g	14.41	6.38	8.91	6.18	3.03

[a] Size of which 10% by weight is smaller.   [b] Ratio of 90% size to 10% size.

TABLE XI

CHARACTERISTICS OF NATURAL WATERS STUDIED

Constituent	Well Water me/l	Tap Water me/l
Na^+	3.6	0.1
Ca^{++}	3.7	0.5
Mg^{++}	5.0	0.3
	12.3	0.9
Cl^-	4.0	0.1
$SO_4^=$	3.6	0.1
HCO_3^-	4.6	0.7
	12.2	0.9

PRELIMINARY YTTRIUM-91 STUDY

One of the difficulties in obtaining meaningful and reproducible data with trace concentrations of the trivalent radionuclides is the sorptive loss of these radioisotopes to the walls of the various containers necessary to an investigation. A further complication is the tendency to form radiocolloids or other non-ionic aggregates and the fact that the distribution of these materials is dependent on time, pH, and probably several other parameters (Ray.[36]).

In order to answer certain of these questions and to eliminate the uncertainty of the role of container surfaces, a simple preliminary experiment was conducted with Y^{91}. Solutions of 0.10 N HCl and 0.10 N NaCl were prepared with equal concentrations of Y^{91} and introduced into gently agitated Pyrex and polyethylene containers. Samples were periodically removed and assayed over a period of about three weeks. A non-agitated control was also included to estimate whether sedimentation might be of significance. The results of this experiment are summarized in Table XII. All counting data have been corrected for decay to a common reference time.

Although the experimental data are not extensive, they do suggest certain characteristics of Y^{91} solutions that may represent a source of error in studying the sorption of this isotope on ion exchange materials. The Y^{91} in acid solution remained substantially constant and presumably in the ionic form at the low pH of 1.7. Even with a pH of 5.50 in 0.10 N NaCl, the reduction of yttrium in solution (or suspension) remained nearly constant, provided the system was agitated. However, with 0.10 N NaCl at a slightly lower pH and under quiescent conditions a steady diminution of Y^{91} in suspension was observed, strongly suggesting the sedimentation of yttrium aggregates. Ray [36] found that colloidal Y^{91} comprised only a few per cent of the activity at pH values less than 5.0, but reached 98 per cent at pH 7 and higher.

TABLE XII

SORPTION OF YTTRIUM-91 ON CONTAINER SURFACES

Solutions	0.10 N HCl	0.10 N NaCl	0.10 N NaCl	0.10 N NaCl
Containers	Pyrex	Pyrex	Pyrex (quiescent)	Poly-ethylene
Measured pH	1.70	5.50	5.40	5.10
Y^{91} in Solution:[a] time in days	cpm/ml	cpm/ml	cpm/ml	cpm/ml
0	1,310	1,310	860	1,310
2	1,310	1,190	455	850
8	1,370	979	510	840
13	---	1,030	340	720
23	1,300	1,220	290	840

[a]Counting coefficients of variation ranged from 5 to 14 per cent.

In the case of the polyethylene system about 40 per cent of the yttrium was associated in some manner with the walls of the container, either as ions or aggregates. Polyethylene would seem to be less satisfactory than Pyrex glass for the purposes of the yttrium investigation.

BATCH EQUILIBRIUM STUDIES--YTTRIUM-91

Although, as noted in an earlier section, slurrying or batch application is less efficient than columns in the use of the exchanger, the batch technique is a useful screening procedure and may also be of scientific interest as a method for investigating sorption equilibria.

Natural Exchangers

A 100-gram sample each of the greensand and the five California agricultural soils were introduced into 500-ml portions of tap water (cf. Table XI) containing Y^{91}. The suspensions were shaken vigorously for five minutes and then allowed to settle for 24 hours before assaying. The results are given in Table XIII. Removals by agricultural soils ranged from 44.7 to 61.7 per cent. Although Oakley sand, with the smallest base exchange capacity, exhibited the smallest yttrium uptake, there was no significant correlation of removal with exchange capacity. The greensand, although it had the highest exchange capacity, gave the lowest yttrium removal--only 5.1 per cent. It is evident that the data obtained did not result from the establishment of a simple ion exchange equilibrium. However, there does appear to be a semblance of correlation between pH and removal, the lower the pH, the higher the removal.

TABLE XIII

REMOVAL OF YTTRIUM-91 BY NATURAL EXCHANGERS--BATCH STUDY[a]

Exchanger	Equilibrium pH	Percentage Removal
Yolo Sandy Loam	7.5	50.3
Hanford Fine Sandy Loam	6.2	61.2
Hesperia Sandy Loam	6.7	52.5
Columbia Sandy Loam	6.3	61.7
Oakley Sand	7.2	44.7
Greensand	7.6	5.1

[a]100 g exchanger in 500 ml tap water.

This experiment clearly indicated the inadequacy of slurrying with soil as a means for removal of yttrium. As the supernatant liquid removed was cloudy, even after 24 hours of settling, a portion of the remaining yttrium may have been associated with the suspended clay and silt materials. The same soils utilized as columns would have provided far better decontamination, as will be shown for greensand in a subsequent paragraph.

Yttrium Distribution Constants

It was of interest to determine whether any consistent relationship existed between the Y^{91} distribution coefficients (k_d or q/c) for the several exchangers and various concentrations of calcium and sodium. Such relationships would be useful in estimating the performance of exchangers exposed to contaminated waters of various characteristics and are of theoretical interest in establishing the order of selectivity of Na^+-Y^{+++} and $Ca^{++}-Y^{+++}$ systems.

Yttrium-91 solutions of 0.001, 0.005, 0.020, and 0.100 normal calcium or sodium chloride were equilibrated with portions of greensand and Duolite C-20 in both the calcium and sodium forms. Duolite A-101 in the chloride form was also equilibrated with a 0.0050 N solution of calcium chloride. The exchangers were first converted to the calcium or sodium form by placing them in columns and then exposing them to an excess of either calcium or sodium chloride solution. The presaturated exchangers were then washed and portions weighed and placed in 125-ml Pyrex Erlenmeyer flasks for the equilibration step. The flasks contained about 2.5 grams of Duolite C-20, 9 grams of greensand, and 1.75 grams of Duolite A-101. Aliquots of 50.0 ml of solution were then added and the flasks gently agitated with periodic radioassaying until equilibrium was reached.

The results of the equilibrium study are given in Table XIV. Both the distribution coefficients and the corresponding decontamination factors (D_F) are shown and may be related by the expression

$$k_d = \frac{q}{c} = (D_F - 1) \frac{V}{v\rho_b} \qquad (10)$$

where V is the volume of solution and $v\rho_b$ the weight of exchanger. Using Equation (10) it is possible to compute the K_{Ca}^Y and K_{Na}^Y mass action "constants" (or, as termed by Helfferich [24], selectivity coefficients) corresponding to the various distribution coefficients reported in Table XIV. However, these have little significance in the context of this experiment as the fraction of yttrium in the trivalent ionic state is unknown and mechanisms other than ion exchange are probably operative in the sorption of the various molecular species of yttrium.

TABLE XIV

INFLUENCE OF CALCIUM AND SODIUM ON YTTRIUM-91 DISTRIBUTION COEFFICIENTS

Exchange System	Solution Normality	Equilibrium pH	k_d	D_F
Na-Duolite C-20 NaCl	0.0010	6.6	7,150	358
	0.0050	6.7	11,800	590
	0.020	6.9	23,800	1,190
	0.100	6.5	39,600	1,980
Na-Greensand NaCl	0.0010	6.7	190	35
	0.0050	6.7	825	150
	0.020	6.8	2,900	523
	0.100	6.5	11,000	1,980
Ca-Duolite C-20 CaCl$_2$	0.0010	5.7	---	---
	0.0050	6.0	11,300	616
	0.020	6.5	18,300	914
	0.100	6.6	9,080	453
Ca-Greensand CaCl$_2$	0.0010	5.9	$> 2.5 \times 10^4$	$> 5 \times 10^3$
	0.0050	5.9	$> 2.5 \times 10^4$	$> 5 \times 10^3$
	0.020	6.6	$> 2.5 \times 10^4$	$> 5 \times 10^3$
	0.100	6.7	3,500	630
Cl-Duolite A101 NaCl	0.0050	6.8	30,600	1,065
Cl-Duolite A101 CaCl$_2$	0.0050	5.8	11,050	374

In the case of both sodium Duolite and sodium greensand, increasing ionic strength resulted in increasing preference of the exchanger for

yttrium. A similar relationship was observed for the calcium systems, but here maxima were evident such that the distribution coefficient was less in 0.10 N calcium solutions than in 0.020 N. These results are in agreement with the findings of Levin, et al. [34] who suggested that at low ionic strengths the equilibrium constant was proportional to some power of the ionic strength. It was also suggested by these authors that the addition of salts might be used to improve decontamination, a measure that certainly would not be practical in the case of emergency drinking water decontamination. Sodium greensand was somewhat less effective than strongly acid resin in the sodium form, but the opposite was true for these exchangers in the calcium form. The large values of the distribution coefficients for the anion resin clearly indicates the presence of negatively charged species of yttrium, probably in molecular combination with the hydroxyl ion. These data further support the work of other researchers regarding the greater effectiveness of mixed-bed systems for removing the trivalent radiocations.

COLUMN DECONTAMINATION STUDIES

The column studies involved the removal of Y^{91} and Ba^{140}-La^{140} from two natural (cf. Table XI) and two synthetic waters through the application of cation and mixed-bed ion exchange columns. Factors such as flow rate, pH, and ionic form of the exchanger were varied in an endeavor to render the results useful on the broadest possible basis in the prediction of decontamination performance.

Procedures

The ion exchange columns were composed of 25 mm inside diameter Pyrex glass packed to an exchanger depth of two feet. In a mono-bed column the Duolite C-20 was employed in the sodium form, while in mixed-bed systems the hydrogen and hydroxyl forms of C-20 and A-101 were employed in equivalent proportions. The greensand was used in its natural form with potassium being the predominant exchangeable cation. The waters to be decontaminated contained either 5 µc/l of Y^{91} or about 10 µc/l of Ba^{140}-La^{140}. These solutions were prepared and stored in polyethylene-lined 55-gallon drums and pumped through Pyrex and Tygon tubing into Pyrex constant-head tanks servicing the exchange columns. Overflow from these tanks was sufficient to agitate the reservoir drums and to minimize the sedimentation of radio-aggregates. Flow through individual columns was controlled by varying the elevation of the point of discharge and thus the head loss across each column. This system also allowed each column to be retained under a positive pressure and thus avoided binding from out-gassing. A photograph of the apparatus is shown in Figure 1.

Generally the influent solutions were allowed to stand in the drums for two or three days to "equilibrate" with the drum liners. Influent radioassays were made at the head-end of each column and showed some variation, but no consistent trend and average values were used to compute column input concentrations. Effluent samples were collected in calibrated gallon bottles with vented stoppers, each containing a small amount of hydrochloric acid to minimize adsorption. Due to the development of a flocculant iron oxide suspension in the well water, it was necessary to introduce a Pyrex glass fiber filter. This filter was periodically replaced and was obviously removing a significant amount of yttrium.
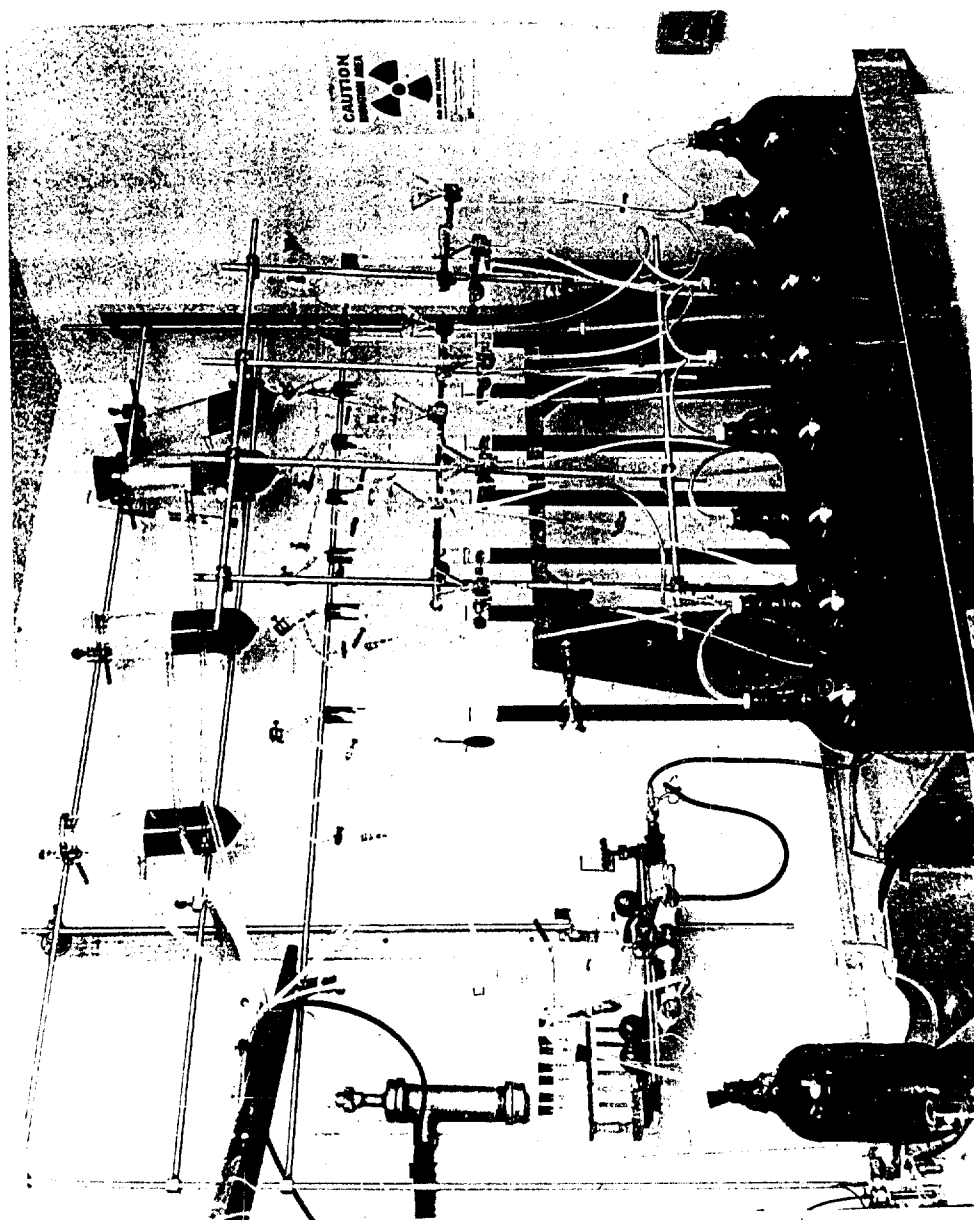
FIGURE I. APPARATUS USED IN COLUMN STUDIES

In the series of Y^{91} runs several hundred pore volumes were passed through each column at a flow rate of about 0.2 gpm/sq ft. The flow rate was then increased to approximately 2.0 gpm/sq ft and the operation continued for a second period with the passage of an additional several hundred pore volumes.

Results of the Yttrium-91 Column Studies

The results of the Y^{91} runs are given in Figures 2 through 5 and summarized in Tables XV and XVI. The effluent data for the mixed-bed systems have not been plotted due to the very low and variable concentrations. Average values are shown in Table XVI. Similar effluent averages have been calculated for the greensand and sodium resin systems and are given in Table XV.

Several significant observations can be made with regard to the yttrium data. Leakage appears to be almost entirely independent of time, there being no evidence that prolonged exposure to radioyttrium resulted in greater passage through the exchanger. However, increasing the flow rate ten-fold did increase leakage in a majority, but not all, cases. It appeared that the influence of flow rate on leakage was less significant with high calcium waters than with sodium waters. Furthermore, the average leakage was appreciably less with the high calcium well water and with 0.005 N $CaCl_2$ than with the low calcium tap water or with 0.005 N NaCl. This was true for both greensand and the sodium resin. In every instance the greensand gave less leakage than the sodium resin. The leakage of yttrium increased with increased pH as has been reported by Ray [36] and other researchers.

It is interesting to note that the distribution coefficients reported in Table XIV for the batch studies indicate that the presence of calcium (at 0.005 N) leads to greater yttrium removal than does sodium, a relationship borne out by the column data. However, the column superiority of greensand was not demonstrated by the batch equilibrium tests. Perhaps the most significant observation is that decontamination factors for yttrium in natural waters passing through cation exchange columns may range from as little as one to not much greater than ten. Greater yttrium removal may be expected from natural waters of relatively great ionic strength, especially in waters containing calcium and magnesium. This conclusion is somewhat anomalous, since normally the selectivity of yttrium over calcium should be less than that of yttrium over sodium. The opposite was observed, probably because the phenomenon was not due to the exchange of trivalent ions.

Mixed-bed resin columns were clearly superior to the single cation exchange column. With well water at a flow rate of 2.2 gpm/sq ft the D_F was 50; with 0.005 N $CaCl_2$, 1,000.

Results of the Barium-Lanthanum-140 Studies

The ten columns used in the Y^{91} study were subsequently employed in the Ba^{140}-La^{140} investigation after flushing each column with sufficient uncontaminated water to insure that no further yttrium leakage could be expected. The conditions and results of the greensand and Duolite C-20
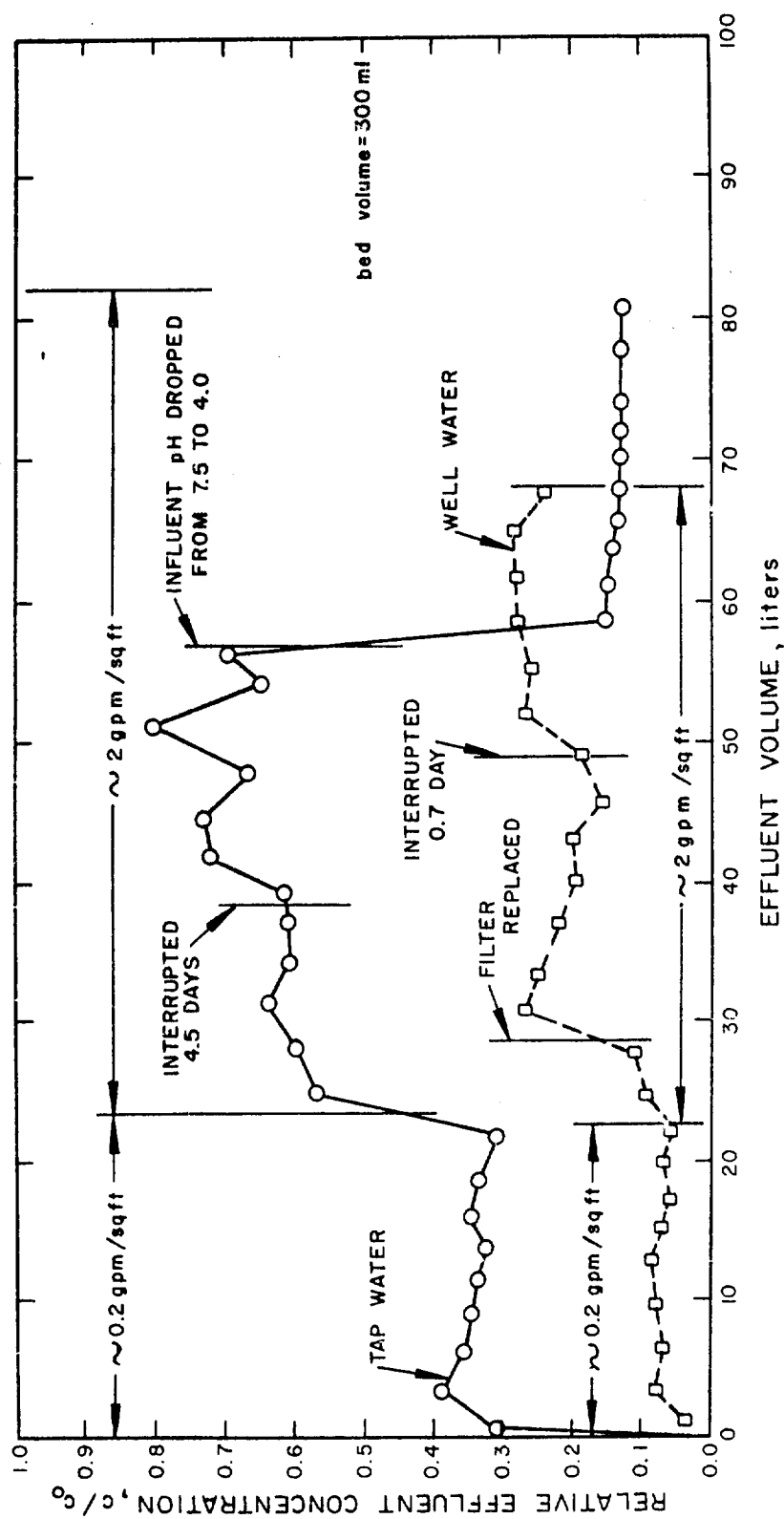
FIGURE 2. YTTRIUM-91 LEAKAGE THROUGH GREENSAND — TAP WATER, WELL WATER
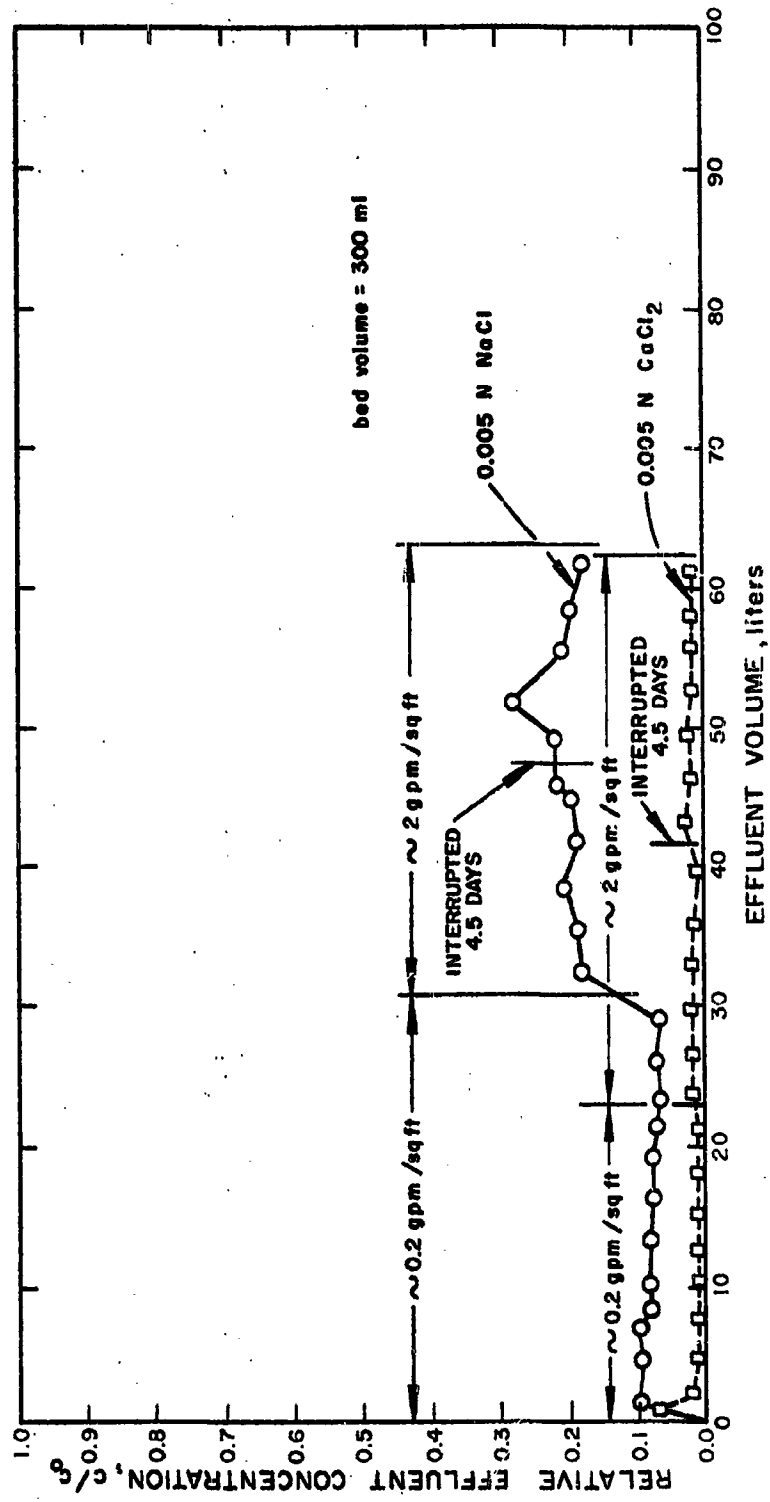
FIGURE 3. YTTRIUM-91 LEAKAGE THROUGH GREENSAND—$NaCl, CaCl_2$
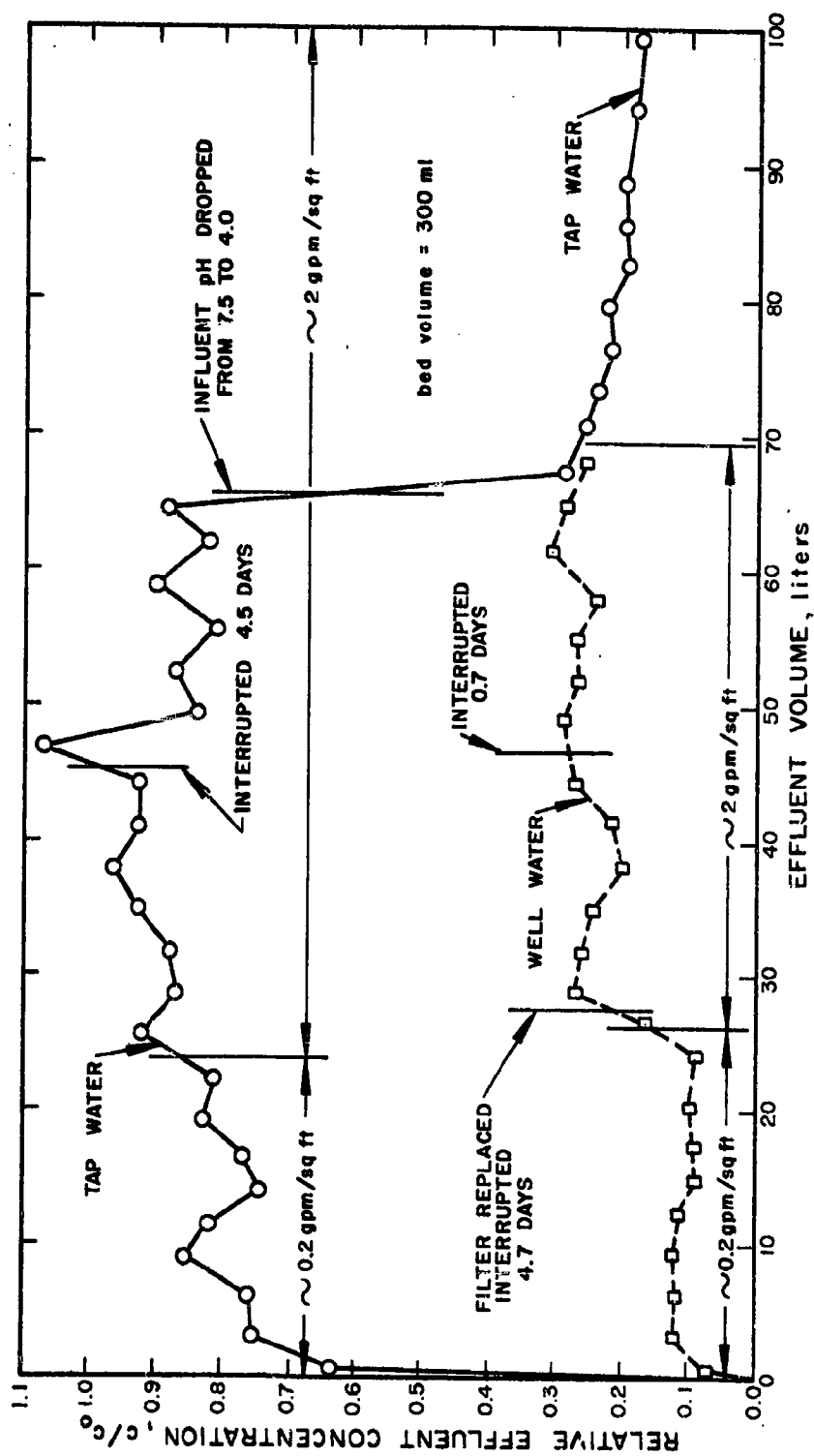
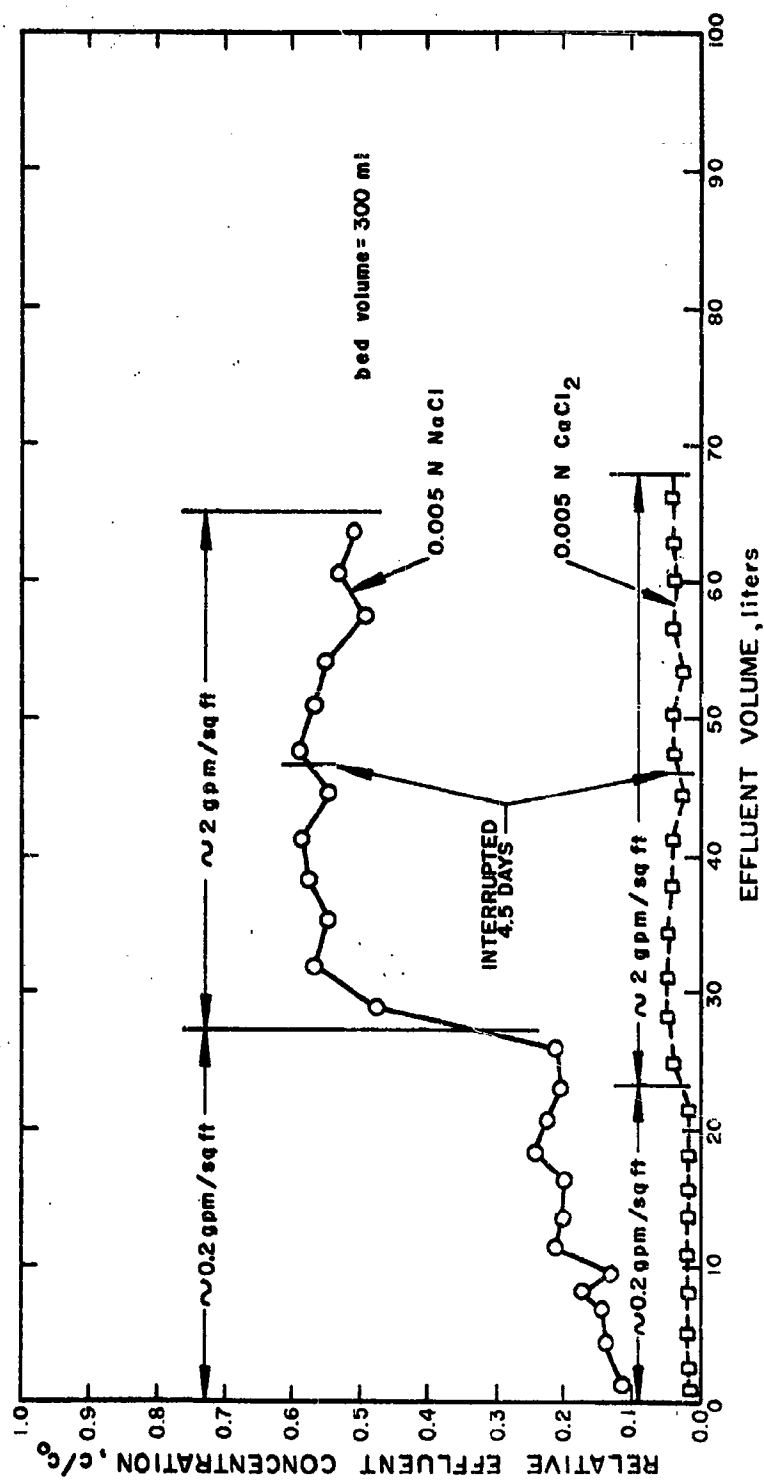FIGURE. 4. YTTRIUM-91 LEAKAGE THROUGH SODIUM RESIN — TAP WATER, WELL WATER

FIGURE 5. YTTRIUM-91 LEAKAGE THROUGH SODIUM RESIN—0.005 N NaCl, 0.005 N CaCl$_2$

TABLE XV

LEAKAGE OF YTTRIUM-91 THROUGH CATION EXCHANGERS

Ion Exchanger Weight, g	Influent Water	pH	Flow Rate 0.22 gpm/sq ft		Flow Rate 1.7-2.2 gpm/sq ft	
			Column Residence Time, min	Effluent Conc., Average, c/c_0	Column Residence Time, min	Effluent Conc., Average, c/c_0
GREENSAND (Glauconite)						
439	Tap	4.0	--	---	3.2	0.14
427	Well	7.1	25	0.08	2.5	0.23
439	Tap	7.5	25	0.34	3.2	0.66
427	0.005 N $CaCl_2$	6.1	25	0.006	2.4	0.018
427	0.005 N NaCl	6.4	25	0.08	2.9	0.20
CATION RESIN (Duolite C-20)						
141	Tap	4.0	--	---	2.6	0.21
141	Well	7.1	25	0.10	2.9	0.26
141	Tap	7.5	27	0.78	2.8	0.90
141	0.005 N $CaCl_2$	6.1	28	0.015	2.9	0.036
141	0.005 N NaCl	6.4	31	0.19	3.0	0.53

TABLE XVI

LEAKAGE OF YTTRIUM-91 THROUGH MIXED-BED RESINS[a]

Influent Water	pH	Dry Weight of Column, g	Flow Rate gpm/ sq ft	Residence Time, min	Effluent Conc., Average, c/c_0
Well Water	8.2	125	0.22 2.2	25 2.5	0.000 0.02
0.005 N $CaCl_2$	6.0	125	0.22 2.2	25 2.5	0.001 0.001

[a] H-Duolite C-20 and OH-Duolite A101.

runs are shown in Figures 6 through 8 and summarized in Table XVII. The barium and lanthanum leakage through the greensand column receiving 0.005 N $CaCl_2$ and NaCl, and the Na-resin column receiving 0.005 N $CaCl_2$ was very small and constant; no figures have been presented, although average leakage values are shown in Table XVII. No significant leakage was observed through the mixed-bed columns, attesting to their superior decontamination capabilities. In several of the column effluents leakage was sufficient to permit the separation of barium and lanthanum by repeated counting and by taking advantage of their different half-lives.

In all instances where barium and lanthanum were separated, leakage of the latter appreciably exceeded the former. Barium leakage was generally small and constant, whereas lanthanum leakage was initially high, but decreased with continued column operation.

Leakage of lanthanum through both greensand and the cation resin was greater for the more mineralized well water than for the tap water. In Table XV yttrium was shown to have exactly the opposite properties. Barium, on the other hand, leaked more when associated with tap water than with well water, but less with 0.005 N $CaCl_2$ than with 0.005 N NaCl. This apparent inconsistency may have been due to the lower pH (5.4) of the $CaCl_2$ solution compared to that of the NaCl solution (7.1). It may be concluded that yttrium and lanthanum are similar to the extent that they form anionic complexes and leak in appreciable concentrations through strongly acidic resins operated in the sodium form. Both are removed to a high degree by mixed-bed systems operating in the hydrogen and hydroxyl forms.

TABLE XVII

LEAKAGE OF BARIUM-140 AND LANTHANUM-140 THROUGH CATION EXCHANGERS

| Ion Exchanger Weight, g	Influent Water	pH	Flow Rate, gpm/ sq ft	Column Residence Time, min	Effluent Conc., Average, c/c_0		
					Ba^{140}	La^{140}	$Ba^{140} + La^{140}$
GREENSAND (Glauconite)							
427	Well	7.3	0.16	44	0.004	0.25^a	
439	Tap	7.4	0.22	29	0.009	0.14	
429	0.005 N $CaCl_2$	5.4	0.20	36			0.000
427	0.005 N NaCl	7.1	0.15	48			0.015
CATION RESIN (Duolite C-20)							
141	Well	7.3	0.21	36	0.016	0.56^a	
141	Tap	7.4	0.18	42	0.027	0.25	
141	0.005 N $CaCl_2$	5.4	0.21	36			0.006
141	0.005 N NaCl	7.1	0.21	37	0.043	0.14	

[a] Initial observation omitted.
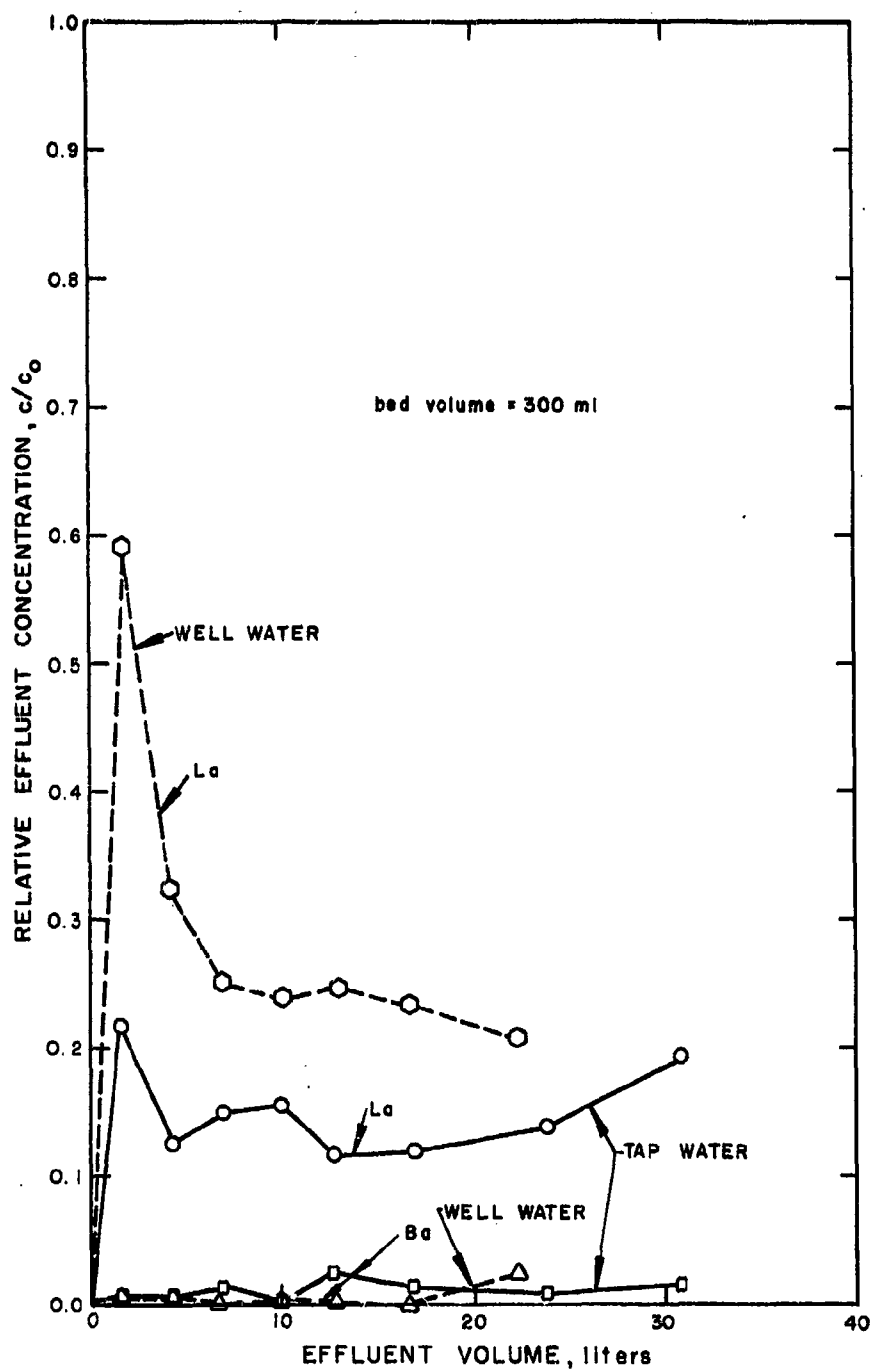
FIGURE 6. BARIUM—LANTHANUM—140 LEAKAGE THROUGH GREEN—
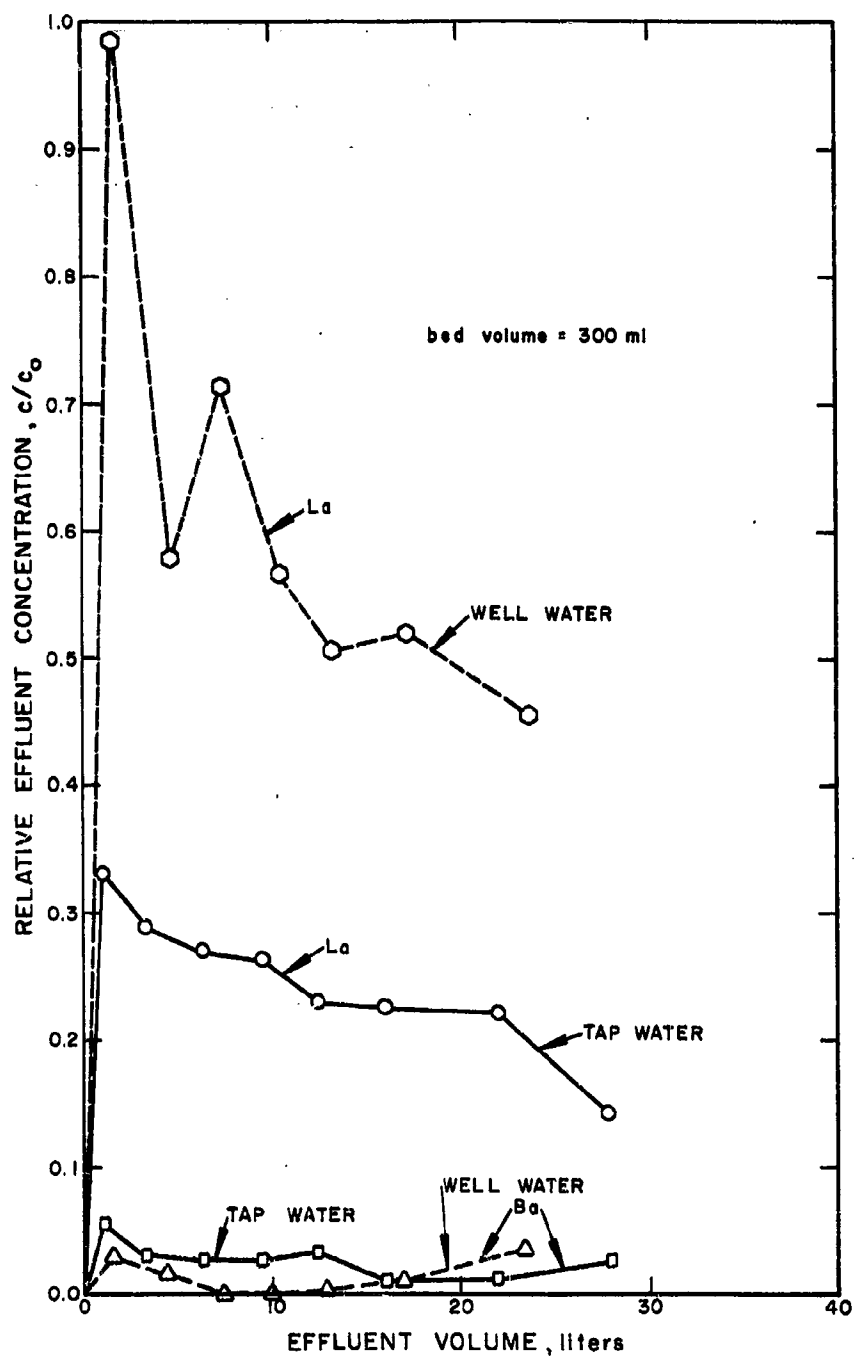SAND—TAP WATER, WELL WATER

FIGURE 7. BARIUM—LANTHANUM—140 LEAKAGE THROUGH SODIUM
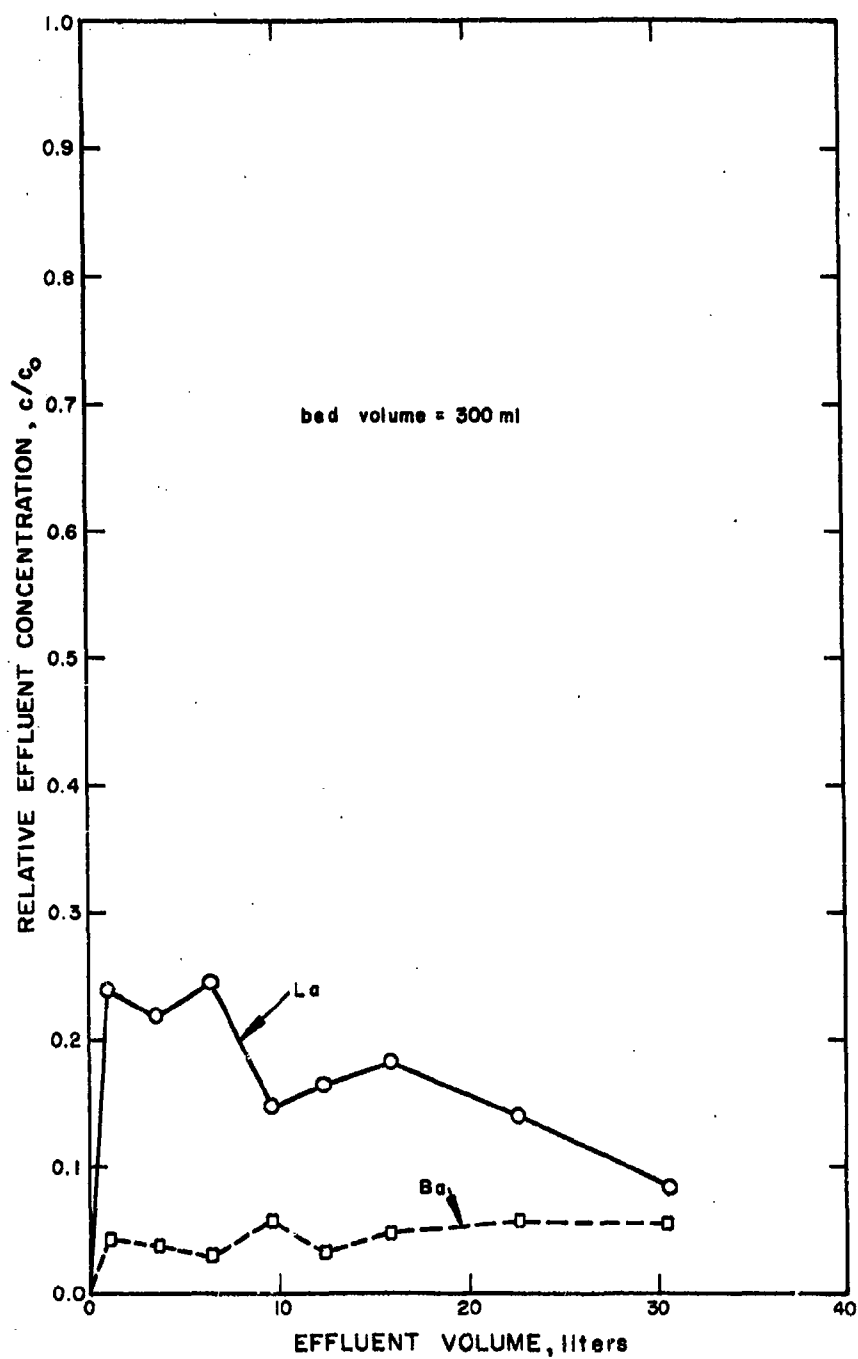RESIN—TAP WATER, WELL WATER

FIGURE 8. BARIUM−LANTHANUM−140 LEAKAGE THROUGH SODIUM
RESIN−0.005 N NaCl

VI. SUMMARY AND CONCLUSIONS

The radiological decontamination of drinking water can be a desirable countermeasure following an attack with nuclear weapons. Although it is difficult to assess the relative contribution of water decontamination to the over-all reduction in radiation exposure of the affected population, it is believed that decontamination measures are feasible and can reduce both the short- and long-term exposure of the population to a degree sufficient to warrant their serious consideration. Obviously the importance of water decontamination will be dependent on local circumstances. Surface supplies having their origin in granitic watersheds and receiving no treatment other than chlorination will be the most vulnerable to radiological contamination; whereas ground-water supplies, properly protected during distribution, will be largely uncontaminated.

Flocculation, sedimentation, and filtration, as commonly practiced for the treatment of surface waters, can remove up to 90 per cent of the radioactivity. Where practiced, lime-soda softening can achieve up to 90 per cent removal of Sr^{89} and Sr^{90}, although such high efficiencies would require more than the normal chemical dosages. Where higher levels of decontamination are required, or where the existing facilities or water characteristics are not suitable for the practice of conventional water softening, ion exchange systems appear to provide an acceptable solution. Ion exchange has the special advantage of simplicity, thus making it adaptable to home applications under the circumstances of a disaster situation.

The experimental work described herein was limited to the radio-isotopes Y^{91} and Ba^{140}-La^{140}. On the basis of these studies, and with a consideration of earlier work reported in the literature, the following conclusions may be made:

1. Both Y^{91} and La^{140} showed a tendency to form anionic aggregates, probably with the hydroxyl ion functioning as a complexing agent or ligand. These aggregates may penetrate considerable distances into cation exchangers. Complex formation increased with increasing pH.

2. The mixed-bed resin systems have clearly superior decontaminating capabilities in comparison to the cationic mono-bed systems. A minimum decontamination factor for Y^{91} of 50 was observed for a 20- to 50-mesh mixed-bed column operated at 2 gpm/sq ft. However, it is reasonable to expect much higher levels of decontamination, perhaps a minimum of about 1000, as typical of mixed-bed systems.

3. Without exception, better decontamination was obtained with acid waters (pH 4 to 6) than with neutral or slightly alkaline waters (pH 7 to 7.5). This is due to the predominance of cations and cationic complexes at greater hydrogen ion concentrations. There was also some indication that superior decontamination may be obtainable with waters of high mineral content than with waters of

low mineral content. Moreover, the presence of the sodium ion appeared to reduce decontamination efficiencies in comparison to the calcium ion.

4. The natural exchanger greensand was superior to the strongly acidic sulfonated polystyrene resin for the removal of Y^{91}, Ba^{140}, and La^{140}. Thus, although the greensand had a much smaller exchange capacity than the synthetic resin, it was capable of providing better decontamination than the resin up to the point of breakthrough. Although the exchange capacity limitation of greensand might be of concern with regard to strontium and cesium removal, it would have little effect on the suitability of greensand for the removal of the rare earths and other trivalent radio-cations. It is quite possible that the admixture of greensand to a synthetic resin would provide an exchange system with the desirable attributes of both exchangers.

5. The slurrying of exchange materials with radioactive solutions containing mono or divalent ions is suitable for the study of ion exchange relationships, but has little practical decontamination value. The use of slurries with the rare earth radioisotopes appears to have little value as a means of screening ion-exchange materials to ascertain their decontamination capabilities. Furthermore, considering the far greater decontamination efficiency and more reliable performance of column systems, it is doubtful if slurrying methods should be recommended for the purpose of radiological decontamination.

6. It is considered feasible to develop an ion exchange decontamination unit that would optimize the various characteristics required for the removal of fission products under the special conditions associated with a nuclear disaster situation. Such an optimization would probably involve the use of both cationic and anionic exchangers in non-equivalent proportions, together with a natural exchanger of the alumino-silicate type. Consideration would also be given to the internal radiological hazard of the various contaminants and the cost of the exchange materials.

APPENDIX

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